CZECHOSLOVAKIA/Chemical Technology - Chemical Products and Their Application. Fats and Oils. Waxes. Soaps and Detergents. Flotation Agents. H.

Abs Jour : Ref Zhur - Khimiya, No 10, 1959, 36662.

Author : Vesely, V., Malenicky, M.
Inst :
Title : Determination of Epihydrine in Glycerin.

Orig Pub : Prumysl potravin. 1957, 9, No 10, 540-541

Abstract : The method of determination of epihydrine with the application of HIO_4 salts was described. The method was introduced into the system of international procedures of the analysis of fats, as the most efficient method for the determination of epihydrine. -- From the authors' resume.

Card 1/1

VESELY, VACLAV

Kapalna paliva. (Vyd.1.) Praha, Statni, nakl.technicke literatury, 1956. 214 p.
(Liquid fuels.)

SO: MONTHLY INDEX OF EAST EUROPEAN ACCESSIONS (EEAI) LC, VOL. 7, NO. 1, Jan. 1958

BAXA, Jozsef, Ing. (Bratislava, Kollarovo namestie, Ceskoslovenska socialisticka republika); VESELY, Vaclav, Prof., ing. (Bratislava, Kollarovo namestie, Ceskoslovenska socialisticka republika)

Oxidation of lubricating oils. Pt. 3. Acta chimica Hung 37 no.2:147-162 '63.

1. Lehrstuhl fur Erdoltechnologie, Slowakische Technische Hochschule, Bratislava, Ceskoslovenska socialisticka republika.

SICHA, M.; VESELY, V.

A study of the propagation of moving striations in inert gases by means of artificial feedback. Chekhosl fiz zhurnal 13 no.9: 662-669 '63.

1. Katedra elektroniky a vakuove fyziky, Karlova universita, Praha.

STUDNICKA, J.; SICHA, M.; VESELY, V.; PROSTEJOVSKY, J.

The effect of stationary stratification on moving striations in a glow discharge in Ne. Chekhosl fiz zhurnal 13 no.1:31-35 '63. (MIRA 16:2)

1. Katedra elektroniky a vakuove fyziky, Karlova universita, Praha.

45590

Z/055/62/012/012/004/004
D256/D308

24,6910

AUTHORS: Šicha, M., Veselý, V., Studnička, J., Prostějovský, J. and Novák, M.

TITLE: Investigation of stationary and traveling striated discharge in neon with local HF excitation

PERIODICAL: Czechoslovak Journal of Physics, v. 12, no. 12, 1962, 919-929

TEXT: The possibility was investigated of using the disturbance produced by a local HF field in systematic studies of stationary and traveling striation of the discharge in inert gases. In the method developed by the authors the HF field interacted upon a limited part of the positive column of a d-c discharge originating stationary and traveling strata and striation waves. Discharge tubes 50 to 80 cm long were used applying across them a voltage adjustable from 200 V to 3 kV. The discharge current was controlled and stabilized with two pentode tubes in series with the discharge tube. The luminous pattern of the discharge was observed visually and tubes

Card 1/3

Investigation of stationary ...

could be moved along and across the discharge tube by means of photoelectronmultiplier. A toroidal resonator operating in the 40 cm wavelength-band provided the local HF excitation. A double structure was observed in the stationary strata differing both in shape and amplitude; the amplitude of one structure against the other one increased with increasing discharge current, but at the same time the stationary strata were independent of the amount of HF power absorbed by the plasma. The striation waves were found to originate in the region of the HF excitation of the positive column. The resonance frequency of the moving strata was investigated as a function of the discharge current as well as the dependence of the wavelength upon the frequency. The frequency of the traveling strata in the striation wave and the resonance frequency of the artificially produced traveling strata were found to be equal within the accuracy of the measurements. The pattern of the discharge could be controlled by changing the modulation of the HF field. It was concluded that the possibility of employing the HF disturbance in the studies of striation in d-c discharges has been established. There are 7 figures and 1 table.

Card 2/3

Investigation of stationary ... Z/055/62/012/012/004/004
D256/D308

ASSOCIATION: Lehrstuhl für Elektronik und Vakuumphysik der Karls-universität, Prag (Department of Electronics and Vacuum Physics, Charles University, Prague) (M. Sicha, V. Veselý, J. Studnička and J. Prostějovský); Physikalisches Institut der Tschechosl. A.d.W., Prag (Institute of Physics, Czechoslovak. AS, Prague) (M. Novák)

SUBMITTED: May 15, 1962

Card 3/3

83383

9.3150

Z/037/60/000/005/016/056
E192/E382

AUTHORS: Bakule, R., Šícha, M., Vesely, V. and Kracík, J.

TITLE: Complex Conductivity of Plasma in a DC Glow Discharge in Neon

PERIODICAL: Ceskoslovensky casopis pro fysiku, 1960, No. 5, p. 408

TEXT: The measurement of the concentration and collision frequency in the positive column of a DC glow discharge in neon by the high-frequency method is described. The results of the measurements show that the expression for the complex conductivity of plasma derived by Fange is applicable to the positive column of a DC glow discharge. It is also shown that the measurements can also be analysed by means of the Lorenz formula which is simpler for numerical calculations. The electron concentration evaluated from this formula is (within the range of experimental error) similr to that calculated from the Fange expression.

ASSOCIATIONS: Katedra elektroniky a vakuové fysiky Karlovy university, Praha (Chair of Electronics and Vacuum Physics of Charles University, Prague)
Fysikální ústav ČVUT, Poděbrady (Physics Institute of ČVUT, Poděbrady.

Card 1/1

Z/055/63/013/001/005/013
E032/E414

AUTHORS: Studnička, J., Šicha, M., Vaněly, V., Prostějovský, J.

TITLE: The effect of stationary stratification on moving striations in a glow discharge in Ne

PERIODICAL: Czechoslovak Journal of Physics, Section B, v.13, no.1, 1963, 31-35

TEXT: The effect of stationary stratification on the parameters of moving striations was investigated with the apparatus described previously (Czech. J. Phys. B 12 (1962), 919). The resonator with which the stratification was excited was supplied with high frequency power which was sufficient to maintain self-supporting high frequency discharge. The high frequency power was modulated with a sine wave derived from a low frequency oscillator. The depth of modulation was sufficient to excite moving striations and was of the order of 10%. The second resonator was placed near the anode and was supplied from a constant amplitude source which was also sufficient to maintain a self-supporting high frequency discharge. Changes in the intensity of the glow in the stationary and moving striations were measured with the aid of a photomultiplier which could be displaced along the discharge tube.

Card 1/3

The effect of stationary ...

The form of the stationary striations was established by measuring the d.c. component of the photomultiplier output which was proportional to the constant component of the radiation emitted by the discharge. The amplitude of the moving striations was determined by measuring the alternating component across a load resistance. The velocity of the moving striations was also determined with the aid of the movable photomultiplier and an oscillograph. Measurement of the amplitude of the moving striations showed that in the region of the maximum of the constant component of the emitted intensity (stationary layers), the amplitude of the alternating component was lower than otherwise. Thus, the moving striations are attenuated at points at which the stationary striations are present. The positions of the minima and maxima in the amplitude of the moving striations are independent of the frequency of the striations but do depend on the structure of the stationary stratification. The velocity of the striations reaches a maximum in the region where the intensity of the constant component of the light flux is a minimum and vice versa. Thus, the results obtained in this work are in agreement

The effect of stationary ... Z/053/63/013/001/005/013
E032/E414

with those reported earlier (Czech. J. Phys. 9 (1959), 495). Moreover, it was found that in the uniform positive column the product of the wavelength of the moving striations and the longitudinal component of the electric field is a constant for each type of moving striations (M. Novák: Czech. J. Phys. B 10 (1960), 954). There are 2 figures.

ASSOCIATION: Katedra elektroniky a vakuové fyziky KU, Praha
(Department of Electronics and Vacuum Physics, Charles University, Prague)

SUBMITTED: May 28, 1962

Card 3/3

Z/055/62/012/011/002/002
D234/D308

AUTHORS: Šicha, M., Veselý, V. and Studnička, J.

TITLE: Artificial excitation of fast moving layers in Ne by a high frequency field

PERIODICAL: Chekhoslovatskiy fizicheskiy zhurnal, Seriya B, v. 12, no. 11, 1962, 873-874

TEXT: Measurements of layer width were carried out in discharge tubes 2 cm in diameter and 50-70 cm long. The width depends linearly on the field frequency. The product of longitudinal electric field strength E on the positive column and the layer width in resonance was computed in order to distinguish between the three layer types (this product is constant for each type). The results show that all three types (p-, r- and s-; L. Pekárek, M. Novak, Czech. J. Phys. 9, 1959, 401) can be excited in Ne. There is 1 figure.

ASSOCIATION: Lehrstuhl für Elektronik und Vakuumphysik der Karlsuniversität, Prag (Department of Electronics and

Card 1/2

Artificial excitation ... 2/055/62/012/011/002/002
D234/D308

Vacuum Physics, Charles University, Prague)

SUBMITTED: May 15, 1962

Card 2/2

Country : Czechoslovakia H-17
Category : Chemical Technology. Chemical Products and Their Applications--Pharmaceuticals. Vitamins. Antibiotics
Abs. Jour. : Referat Zhur--Khim., No 11, 1959, 39640

Author : Vesely, V.
Institut. : Not given
Title : Dyes for Parenteral Use in Diagnosis

Orig Pub. : Farmacia (Czechoslovakia), 27, No 8, 242-245 (1958)

Abstract : The preparation of sterile ampules with bilirubin, taurobilirubin, bromosulfophthalein, Congo Red, Trypan Blue, 4,4-bis-[(7),1-amino-8-hydroxy-2,4-disulfo-(Naphthylazo)]-3,3-bitolyl [spelling?] and their application for diagnostic purposes is described.

I. Matveyeva

Card: 1/1

BAXA, J.; GRUBA, G.; KUBICZKOVA, H.; VESELY, V.

Oil oxidation. Part 2: Oxidation process and products. Ropa a uhlie 5 no.1:7-11 Ja '63.

1. Katedra chemie a technologie ropy, Slovenska vysoka skola technicka, Bratislava.

VESELY, Vaclav

Corrosion in crude oil processing. Ropa a uhlie 5 no.6: 164-165 Je '63.

1. Katedra chemie a technologie ropy, Slovenska vysoka skola technicka, Bratislava.

VESELY, Vaclav, prof., inn.

"Chemical processing of natural gas hydrocarbons", by M. Hrusovsky. Reviewed by Vaclav Vesely. Chem. zvesti 16 no.8:644 Ag '62.

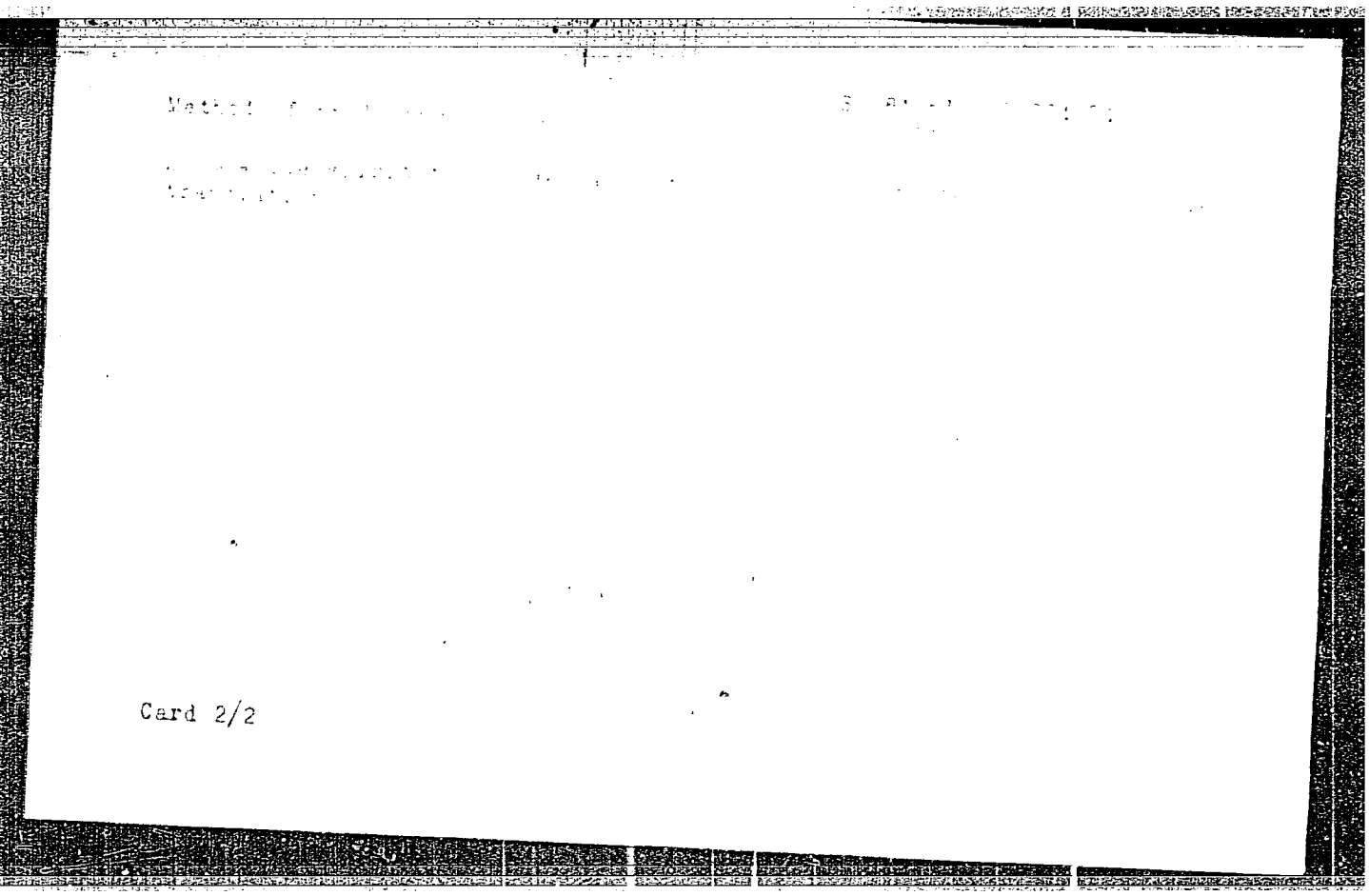
S/081/63/000/004/040/051
B160/B180

AUTHORS: Štěpina, Václav, Veselý, Václav, Čejka, František

TITLE: Method of producing engine oils for two-stroke gasoline engines

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 4, 1963, 536, abstract 4P262 (Czech. pat. 103403, Jan. 15, 1962)

TEXT: An engine oil for two-stroke gasoline engines, which is introduced into the engine mixed with the gasoline is produced from the aromatic extract from selective-refined mineral oils by using propane extraction to remove the polycyclic compounds from the extract, adsorption refining, H_2SO_4 refining or cyclofining. The [illegible] compounds can be removed from the extract [illegible] solvent such as white spirit, [illegible] refined extract [illegible] this way is used as [illegible] example a petrol extract (viscosity 38° Ost [illegible] white spirit [illegible] 75 ost 50°C and then refined with [illegible] H_2SO_4, lixiviated, washed with water [illegible] dried [illegible] obtained as [illegible] % oil and [illegible].



Card 2/2

Z/032/63/013/001/003/004
B073/B186

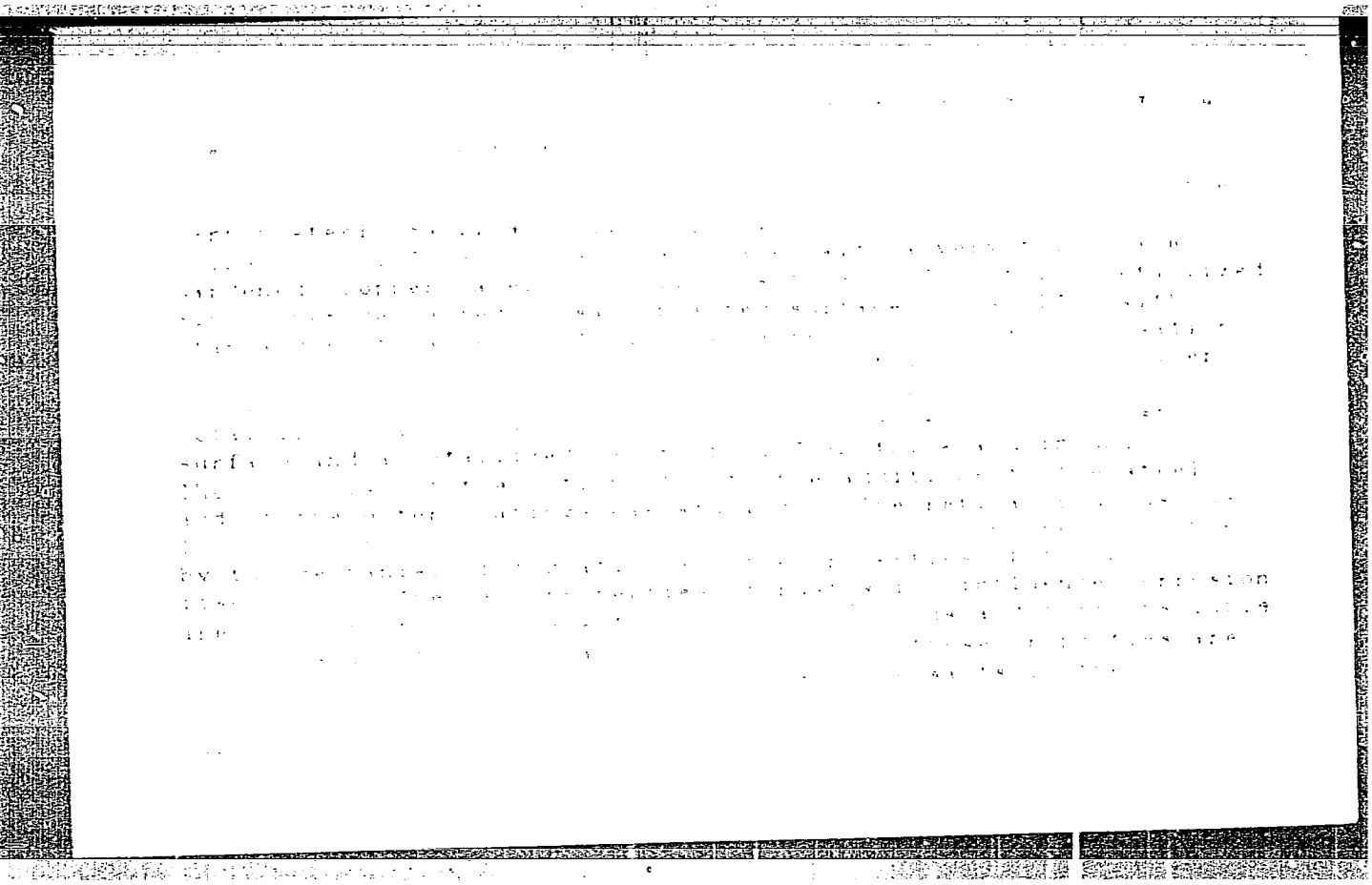
AUTHORS: Barton, K., Engineer, Veselý, V., Candidate of Sciences, Engineer, Oráč, O.

TITLE: New method of improving the resistance of steel to atmospheric corrosion

PERIODICAL: Strojírenství, v.13, no.1, 1963, 46-51

[illegible] effective alloying element for inhibiting atmospheric corrosion [illegible] steels, steels of [illegible] are not produced in [illegible]

[illegible]



APPROVED FOR RELEASE: 09/01/2001 CIA-RDP86-00513R001859620008-2"

practical conclusions: 1) The action of alloying additions in low-alloy steels can be simulated by a thin, porous coating of zinc for any other metal capable of forming stable alkaline salts,

Stavomontáže, Banská Bystrica (Z.Krajíc, S.Urák)

Card 4/4

VESELY, Vladimir, inz.

Further water deactivation methods. Vodni hosp 13 no.6:213-214 '63.

1. Ustav jaderneho vyzkumu, Rez.

VESELY, V., inz.

Radioisotopes in water conservation and water purification. Vodni hosp 13 no.6:239-240 '63.

VESELY, V.; MALENICKY, M.; POKORNY, J.

Report on the meeting of the Section Fats of the International Union of Pure and Applied Chemistry in Prague. Chem listy 57 no.1:103 Ja '63.

VESELY, Vladimir

Desiccation of fondant sweets and fillings. Listy cukrovar 80 no.10:269-274 O '64.

1. Research Worksite of the Ceskoslovenske cokoladovny National Enterprise in Bratislava.

VESELY, Vladimir

Possibility of continuous production of jelly. Listy cukrovar 79 no.4:93-97 Ap '63.

BERANOVA, Hana; MALY, Jaromir; VESELY, Vaclav

Uranyl nitrate extraction by tributyl phosphate. Jaderna energie 4 no.6:145-148 Je '58.

1. Ustav jaderne fysiky, Ceskoslovenska akademie ved, Praha.

Vesely, V.

CZECHOSLOVAKIA/Nuclear Physics - Nuclear Engineering and Power. C-8

Abs Jour : Ref Zhur - Fizika, No 1, 1958, 643

Author : Vesely, V., Zaruba, J.
Inst : -
Title : Deactivation of Liquid Radioactive Wastes.

Orig Pub : Jaderna energie, 1957, 3, No 5, 147-151

Abstract : Survey article.

Bibliography, 14 titles.

Card 1/1

H-5

Country : Czechoslovakia
Category :

Abs. Jour. : 39118

Author : Vesely, V. and Zaruba, J.
Institut. : Not given
Title : The Decontamination of Radioactive Waste Waters

Orig Pub. : Jaderna Energie, 3, No 5, 147-151; No 6, 180-187 (1957)

Abstract : A review article with a bibliography listing 30 titles.

Card: 1/1

VESELY, V. ; NAPRAVNIK, J.

Measurement of very low radiation activity in water.

P. 406. (JADERNA ENERGIE) (Praha, Czechoslovakia) Vol. 3, no. 12, Dec. 1957

SO: Monthly Index of East European Accession (EEAI) IC Vol. 7, No. 5, May 1958

VESELY, V.

Distr: 4E2c

Sodium polyuranate chemistry. Jaromir Maly and Vaclav Vesely (Inst. Nuclear Phys., Prague). *J. Inorg. & Nuclear Chem.* 7, 119–28(1958).—Forward and reverse potentiometric titration of NaOH and uranyl nitrate solns. showed polyuranates with different Na:U ratios and one with the empirical formula $(UO_3H_2O)_3N_2O_3$ (I). Changes in absorption spectra and pH indicated polymerization and hydrolysis of uranyl ions in titrations, and this was correlated with compn. I and $(UO_3H_2O)_nNa_2O$ (n = 3–16) were obtained as solids; I, and the n = 5 and 16 Na salts have similar orthorhombic structures, a = 7.09 ± 0.02, b = 9.55 ± 0.02, and c = 5.11 ± 0.06A. For polyuranates with n <5, the structure was different and the following spacings were established by powder diffraction: 5.843, 4.136, 3.397, 3.200, 2.985, 2.699, 2.505, 2.260, 1.985, 1.888, 1.729, 1.417, 1.352, 1.288, 1.123, and 1.070A. Jack J. Bulloff

VESELY, Vaclav

C

COUNTRY : Czechoslovakia
CATEGORY : Inorganic Chemistry. Complex Compounds.

ABS. JOUR. : RZKhim., No. 16 1959, No. 56616

AUTHOR : Maly, J. and Vesely, Vaclav.
INST. : Not given Inst. Nuclear Physics, Prague
TITLE : Note on the Chemistry of the Sodium Polyuranates

ORIG. PUB. : Jaderna Energie, 4, No 12, 371-376 (1958)

ABSTRACT : Polyuranates have been prepared by the reaction of solutions of NaOH with $UO_2(NO_3)_2$. The formation of polyuranates with varying Na/U ratios was established by potentiometric titration. The absorption spectra and pH measurements show polymerization and hydrolysis of the $UO_2(2+)$ ions. Crystalline $(UO_3 \cdot H_2O)_5 \cdot N_2O_5$ (I) and $(UO_3 \cdot H_2O)_n \cdot Na_2O$ (II), with n = 3-16, have been isolated. The x-ray data for I and II (n = 5,16) indicate a rhombic structure with lattice parameters a = 7.09 ± 0.02, b = 9.55 ± 0.02, and c = 5.11 ± 0.02A. From authors' summary

CARD: 1/1

60

Country : CZECHOSLOVAKIA B
Category : Analytical Chemistry. Analysis of Inorganic Substances
Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15086

Author : Cepelak, J.; Maly, J.; Vesely, V.
Institut. : -
Title : Determination of Uranyl Nitrate in the Presence of Free Nitric Acid by Alkalimetric Titration

Orig Pub. : Chem. listy, 1958, 52, No 3, 547-549

Abstract : On the basis of the reaction: $UO_2(NO_3)_2 + H_2O_2 = 2HNO_3 + UO_4$, which proceeds quantitatively at pH 2-5, a rapid titrimetric method was developed for the determination of $UO_2(NO_3)_2$ (UN), which is also effective in the presence of free HNO_3. Elimination of excess H_2O_2 during titration is not required. An outlay of 0.1 n. NaOH, the equivalent of freed HNO_3, is established potentiometrically or visually. The potentio-

Card: 1/5

Country : CZECHOSLOVAKIA
Category : Analytical Chemistry. Analysis of Inorganic Substances
Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15086

Author :
Institut. :
Title :

Orig Pub. :

Abstract Cont'd : metric method consists in first titrating the total HNO_3 after the addition of 5 ml. of 30% H_2O_2 to the analyzed solution, and then titrating the free acid without the addition of H_2O_2; from the difference, the quantity of UN present is found. An accurate reading of the inflection point on the titration curve of free HNO_3 is hindered by the appearance of a second inflection point which corresponds to the formation of $UO_2(UO_3)_4(NO_3)_2$. Therefore, it is

Card: 2/5

E - 22

E

Country : CZECHOSLOVAKIA
Category : Analytical Chemistry. Analysis of Inorganic Substances
Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15086

Author :
Institut. :
Title :

Orig Pub. :

Abstract Cont'd : recommended to add 3 g. of hard $NaNO_3$ per each 0.5 g. of UN to the analyzed solution, before titration without H_2O_2, in order to suppress the hydrolytic formation of $UO_2(UO_3)_4(NO_3)_2$.

In visual determination of the terminal point, the total quantity of HNO_3 (1-2.5 g. of UN per 100 ml.) is titrated first after the addition of H_2O_2 and 10 drops of Tashiro indicator (100 ml. of 0.03% alcohol solution of methyl red

Card: 3/5

E

Country : CZECHOSLOVAKIA
Category : Analytical Chemistry. Analysis of Inorganic Substances
Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15086

Author :
Institut. :
Title :

Orig Pub. :

Abstract Cont'd : plus 15 ml. of 0.1% aqueous solution of methylene blue) up to a change of the violet color of the solution into yellow-green; then, the free HNO_3 is titrated according to a mixed indicator (70 ml. of 0.1% alcohol solution of dimethyl yellow plus 30 ml. of 0.1% solution of methylene blue) until change of the cherry-red color into green. The visual method of determining the end of titration is simpler and faster than the potentiometric one, and gives

Card: 4/5

Country : CZECHOSLOVAKIA E
Category : Analytical Chemistry. Analysis of Inorganic Substances
Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15086

Author :
Institut. :
Title :

Orig Pub. :

Abstract Continued : more accurate results. The average error of differential determination of UN is less than ± 2%.-- J. Vanecek

Card: 5/5

S/081/62/000/024/008/073
B108/B186

AUTHORS: Beranová, H., Lenk, R., Malý, J., Veselý, V.

TITLE: Extraction of the main fission products of uranium by means of some ketones from acid solution and from solution with acid deficiency

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 24, 1962, 78, abstract 24B546 (Collect. Czechosl. Chem. Communs, v. 27, no.2, 1962, 487 - 491 [Ger.; summary in Russ.])

TEXT: Measurements were taken of the distribution coefficients of Sr^{90}, Zr^{95}, Ru^{106}, Ce^{144}, and Cs^{137} between the aqueous solutions of 0.25M $UO_2(NO_3)_2$, 5M NH_4NO_3, of various concentrations with respect to HNO_3, and $CH_3COC_5H_{11}$ (I), $CH_3CO\text{-iso-}C_4H_9$ (II), $CH_3COC_3H_7$ (III), and methyl cyclohexanone (IV). The extraction of Cs^{137} and Ce^{144} by all of the solvents and the extraction of Sr^{90} by III and IV depends but little on the acid concentration. On extraction with I and II, the distribution coefficient

Card 1/2

Extraction of the main fission ...

of Sr^{90} decreases by two orders of magnitude when the HNO_3 concentration is reduced from 3M to zero. The extraction of Zn^{95} and Ru^{106} is reduced sharply on transition from acid solutions to solutions with acid deficiency. For the previous paper, see RZhKhim, 1961, 22V7. [Abstracter's note: Complete translation.]

Card 2/2

VESELY, V.; BERANOVA, H.; MALY, J.

Extraction of irradiated uranium by ketones in acid solutions and acid-poor solutions. Coll Cz chem 25 no.10:2622-2629 O '60. (EEAI 10:9)

1. Institut fur Kernforschung, Tschechoslowakische Akademie der Wissenschaften, Prag.

(Extraction(Chemistry)) (Ketones) (Uranium) (Solutions)

VESELY, Vladimir; JENICEK, Alois; DRAHOZAL, Josef

Radioactive waste disposal plant in the Nuclear Research Institute. Jaderna energie 9 no.1:3-7 Ja '63.

1. Ustav jaderneho vyzkumu, Ceskoslovenska akademie ved (for Vesely). 2. Chemoprojekt (for Jenicek and Drahozal).

VESELY, V.

TECHNOLOGY

periodicals: JADERNA ENERGIE Vol. 4, No. 12, Dec. 1958

MALY, J; VESELY, V. Contribution to the sodium polyuranate chemistry. p. 371.

Monthly List of East European Accessions (EEAI) LC VOL. 8, no. 5 May 1959, Unclass.

VESELY, V., inz.; ZARUBA, J., inz.

Disposal of radioactive waste water. Jaderna energie 3 no.5:147-151 My '57.

1. Ustav jaderne fysiky, Ceskoslovenska akademie ved, Praha.

VESELY, V., inz.; ZARUBA, J., inz.

Disposal of radioactive waste water. Jaderna energie 3 no.6:180-187 Je '57.

1. Ustav jaderne fysiky, Ceskoslovenska akademie ved, Praha.

VESELY, V.

"Atomic energy waste, its nature, use, and disposal." Reviewed by V.Vesely. Jaderna energie 7 no.9:324 S '61.

VESELY, S.

BC

B1

Application of the electron-microscope to metallography. M. Rozsival, S. Vesely, and J. Chodorowski (*Prace Gldam. Dadaw. Inst. Met. Ostrawie*, 1950, 2, 81—87; *Metal Abstr.*, 1951, 18, 523).—A series of photographs of various metallurgical structures (hardened and tempered steels, age-hardened steels, and light alloys and ppt. formed during heat-treatment and cold-working) showing the comparison between optical micrographs at various magnifications and electron-micrographs is presented. Cr-shadowed Formvar is used as the main replica but some results with all-metal replicas are shown. These were made by evaporating Cr on to intermediate replicas of methyl methacrylate or *polystyrene* and dissolving away the plastic. Full metallographic details are given. R. B. CLARKE.

(3) 4

VESELY, V.; BAXA, J.

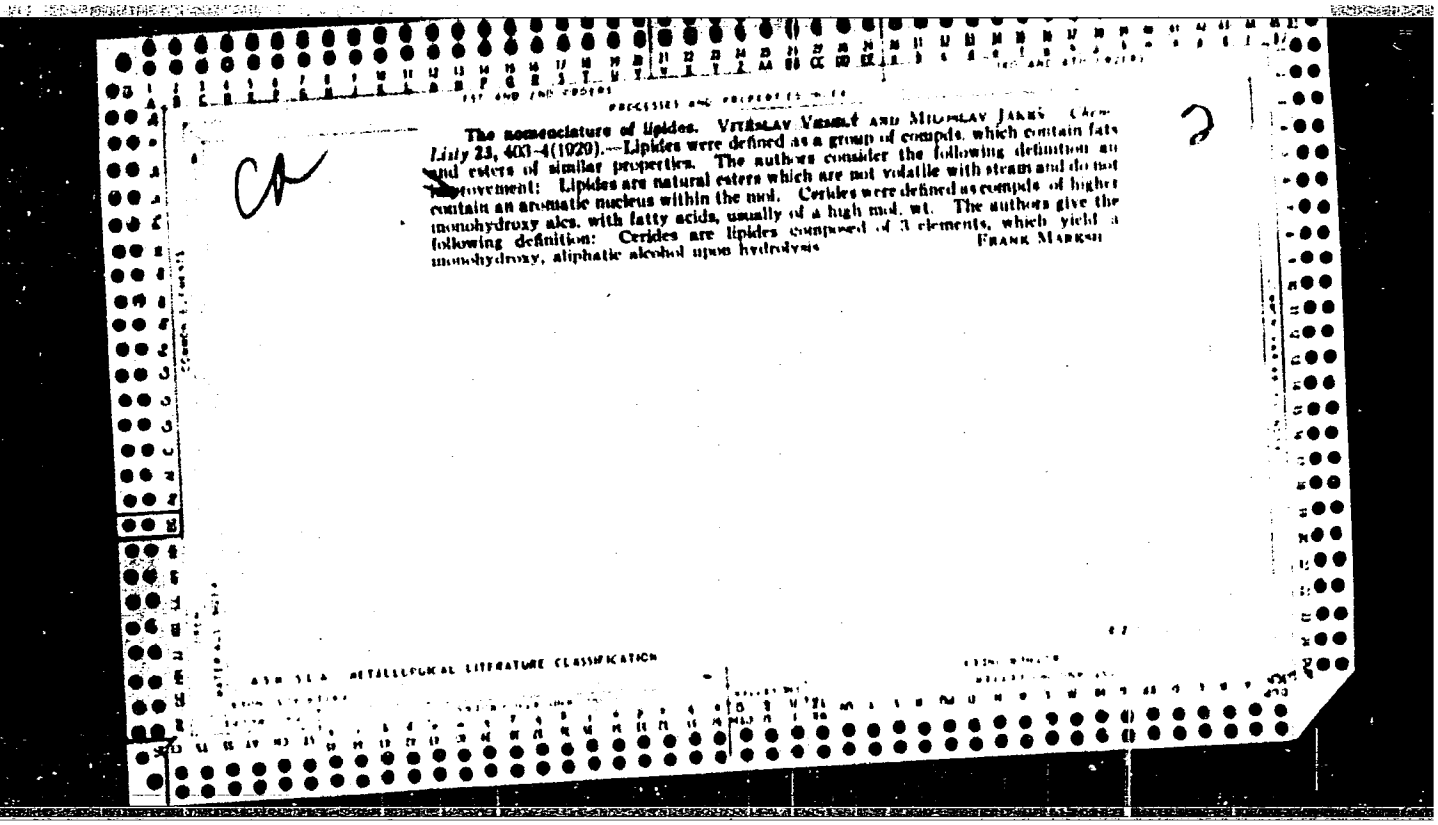
Oxidation stability of hydrogenated lubricating oils. Pt.5.
Ropa a uhlie 7 no.3:65-72 Mr '65.

1. Chair of Petroleum Chemistry and Technology of the Faculty of Chemistry of the Slovak Higher School of Technology, Bratislava.

GURSKY, Juraj; VESELY, Vaclav

Detonation properties of gasolines and antiknock components. Pt.2. Ropa a uhlie 7 no.2:53-57 F '65.

1. Chair of Petroleum Chemistry and Technology and Chair of Chemical Engineering Processes and Equipment of the Slovak Higher School of Technology, Bratislava.



The nomenclature of lipides. VITĚZSLAV VEJDĚLEK AND MILOSLAV JANKŮ (Chemotechnika) *Listy* 23, 403–4(1929).—Lipides were defined as a group of compds. which contain fats and esters of similar properties. The authors consider the following definition an improvement: Lipides are natural esters which are not volatile with steam and do not contain an aromatic nucleus within the mol. Cerides were defined as compds. of higher monohydroxy alcs. with fatty acids, usually of a high mol. wt. The authors give the following definition: Cerides are lipides composed of 3 elements, which yield a monohydroxy, aliphatic alcohol upon hydrolysis. FRANK MARKUS

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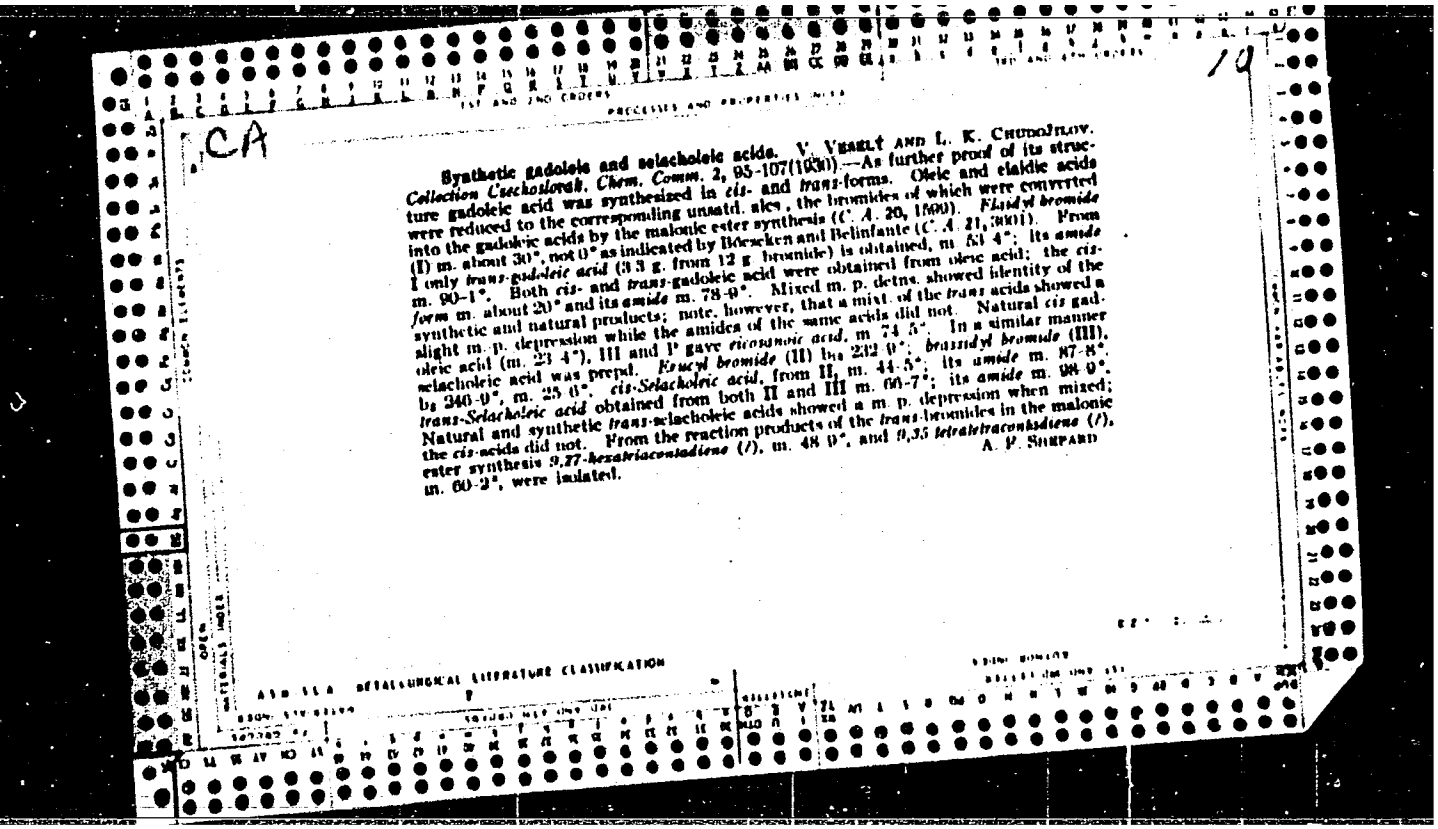
Mononitro and monoamine derivatives of 1-methylnaphthalene. V. Veselý, F. Šturma, H. Olejníček and K. Rein. *Collection Czechoslov. Chem. Commun.* 1, 493-515 (1929).—1-$C_{10}H_7Me$ (I) was nitrated with fuming HNO_3 in glacial HOAc, giving *1-methyl-4-nitronaphthalene* (II), m. 68-69°, and an oil consisting of isomeric $C_{10}H_6(NO_2)Me$. Reduction with Pt black and H_2 and acetylation of the amines show this oil to be mostly II. Part of this oil resisted catalytic reduction, and was found to contain 1,2-$C_{10}H_6(NO_2)Me$, from 2-$C_{10}H_7Me$ present as an impurity in I. This oil contained also *1-methyl-8-nitronaphthalene*, shown by reduction with $SnCl_2$ and HCl and acetylation to give *1-methyl-8-acetylaminonaphthalene*, m. 183-4°. Five g 1,2,4-$C_{10}H_5Me(NO_2)_2$ (III) (cf. *C. A.* 20, 2325), on partial reduction with Pt and H_2, and crystn. from alc. gave 1 g. *1-methyl-2-nitro-4-aminonaphthalene* (IV), m. 131-2°. IV is formed from III also by treatment with NH_4SH. IV, on diazotization and decompn. with boiling alc., gave *1-methyl-2-nitronaphthalene* (V), m. 80-8°. V, on reduction with Zn powder and HOAc, gave *1-methyl-2-aminonaphthalene* (VI), m. 40-50°; *Ac deriv.*, m. 188-9°; *Bz deriv.*, m. 222°. Fourteen g. 1,4-$C_{10}H_6MeNHAc$ (cf. *C. A.* 8, 901) treated with fuming HNO_3 in glacial HOAc, and crystn. of the product from alc. gave 9.5 g. *1-methyl-3-nitro-4-acetylaminonaphthalene* (VII), m. 234-5°. Eight g. VII, heated with alc. and concd. HCl, gave 5.5 g. *1-methyl-3-nitro-4-aminonaphthalene* (VIII), m. 179.5°, which forms no salt with concd. HCl. VIII was diazotized in HOAc-H_2SO_4, and decompd. with boiling alc. to give *1-methyl-3-nitronaphthalene* (IX) (2.1 g. from 6 g. VIII), m. 81-2°. Reduction of IX with Fe filings and HOAc gave *1-methyl-3-aminonaphthalene* (X), m. 68°; *Ac deriv.*, m. 172-3°; *Bz deriv.*, m. 104-5°. Diazotization of X, and warming with H_2SO_4 gave *1-methyl-3-hydroxynaphthalene*, m. 80-1°. Reduction of VIII with $SnCl_2$ gave *1-methyl-3,4-diaminonaphthalene*, m. 91°. I (319 g.) treated cold with $ClSO_3H$ and subsequent neutralization with K_2CO_3 and steam distn. gave 370 g. of K *1-methylnaphthalene-4-sulfonate* (XI) and 75 g. consisting mainly of isomeric salts

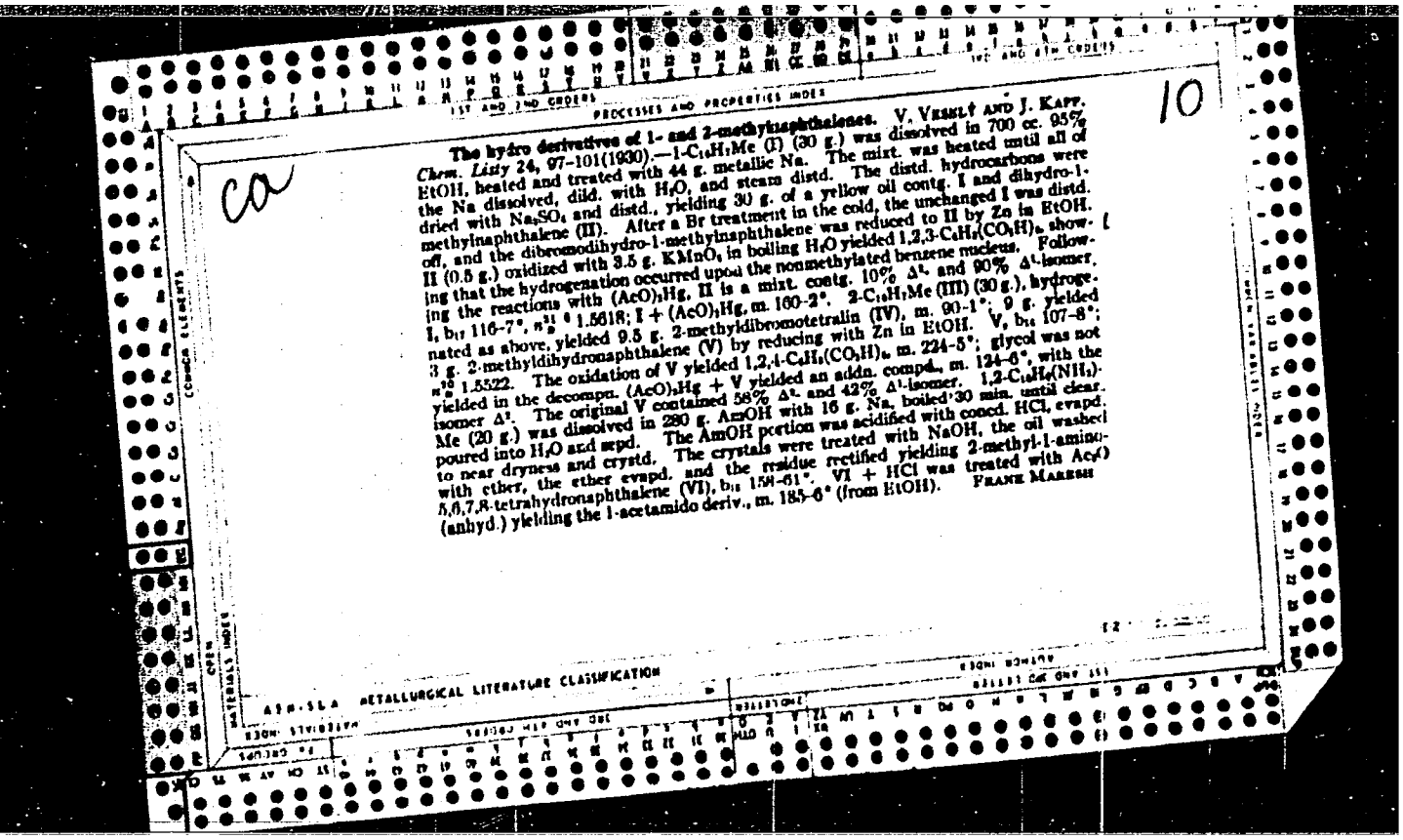
ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



CA

Synthetic gadoleic and selacholeic acids. V. Vesely and L. K. Chodounsky. *Collection Czechoslovak. Chem. Comm.* 2, 95-107(1930).—As further proof of its structure gadoleic acid was synthesized in *cis*- and *trans*-forms. Oleic and elaidic acids were reduced to the corresponding unsatd. alcs., the bromides of which were converted into the gadoleic acids by the malonic ester synthesis (*C. A.* 20, 1660). *Elaidyl bromide* (I) m. about 30°, not 0° as indicated by Böeseken and Belinfante (*C. A.* 21, 3001). From I only *trans-gadoleic acid* (3.3 g. from 12 g. bromide) is obtained, m. 85.4°; its *amide* m. 90–1°. Both *cis*- and *trans*-gadoleic acid were obtained from oleic acid; the *cis*-*form* m. about 20° and its *amide* m. 78-9°. Mixed m. p. detns. showed identity of the synthetic and natural products; note, however, that a mixt. of the *trans* acids showed a slight m. p. depression while the amides of the same acids did not. Natural *cis* gadoleic acid (m. 23.4°), III and P gave *eicosanoic acid*, m. 74.5°. In a similar manner selacholeic acid was prepd. *Eicosyl bromide* (II) b_{15} 232.0°; *brassidyl bromide* (III), b_5 240-0°, m. 25.0°. *cis-Selacholeic acid*, from II, m. 44.5°; its *amide* m. 98.0°. *trans-Selacholeic acid* obtained from both II and III m. 60-7°; its *amide* m. 98.0°. Natural and synthetic *trans*-selacholeic acids showed a m. p. depression when mixed; the *cis*-acids did not. From the reaction products of the *trans*-bromides in the malonic ester synthesis *9,27-hexatriacontadiene* (*I*), m. 48.0°, and *9,35 tetratetracontadiene* (*I*), m. 60-2°, were isolated.

A. P. Sharpe



PROCESSES AND PROPERTIES INDEX

10

ca

The hydro derivatives of 1- and 2-methylnaphthalenes. V. Vesely and J. Kapp. *Chem. Listy* 24, 97–101(1930).—1-$C_{10}H_7Me$ (I) (30 g.) was dissolved in 700 cc. 95% EtOH, heated and treated with 44 g. metallic Na. The mixt. was heated until all of the Na dissolved, dild. with H_2O, and steam distd. The distd. hydrocarbons were dried with Na_2SO_4 and distd., yielding 30 g. of a yellow oil contg. I and dihydro-1-methylnaphthalene (II). After a Br treatment in the cold, the unchanged I was distd. off, and the dibromodihydro-1-methylnaphthalene was reduced to II by Zn in EtOH. II (0.5 g.) oxidized with 3.5 g. $KMnO_4$ in boiling H_2O yielded 1,2,3-$C_6H_3(CO_2H)_3$, showing that the hydrogenation occurred upon the nonmethylated benzene nucleus. Following the reactions with $(AcO)_2Hg$, II is a mixt. contg. 10% Δ^1- and 90% Δ^2-isomer. I, b_{15} 116–7°, n_D^{21} 1.5618; I + $(AcO)_2Hg$, m. 160–2°. 2-$C_{10}H_7Me$ (III) (30 g.), hydrogenated as above, yielded 9.5 g. 2-methyldibromotetralin (IV), m. 90–1°. 9 g. yielded 3 g. 2-methyldihydronaphthalene (V) by reducing with Zn in EtOH. V, b_{15} 107–8°; n_D^{20} 1.5522. The oxidation of V yielded 1,2,4-$C_6H_3(CO_2H)_3$, m. 224–5°; glycol was not yielded in the decompn. $(AcO)_2Hg$ + V yielded an addn. compd., m. 124–6°, with the isomer Δ^2. The original V contained 58% Δ^2- and 42% Δ^1-isomer. 1,2-$C_6H_4(NH_2)$-Me (20 g.) was dissolved in 280 g. AmOH with 16 g. Na, boiled 30 min. until clear, poured into H_2O and steam distd. The AmOH portion was acidified with concd. HCl, evapd. to near dryness and crystd. The crystals were treated with NaOH, the oil washed with ether, the ether evapd. and the residue rectified yielding 2-methyl-1-amino-5,6,7,8-tetrahydronaphthalene (VI), b_{15} 158–61°. VI + HCl was treated with Ac_2O (anhyd.) yielding the 1-acetamido deriv., m. 185–6° (from EtOH). Franz Marsch

A.S.M.-S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

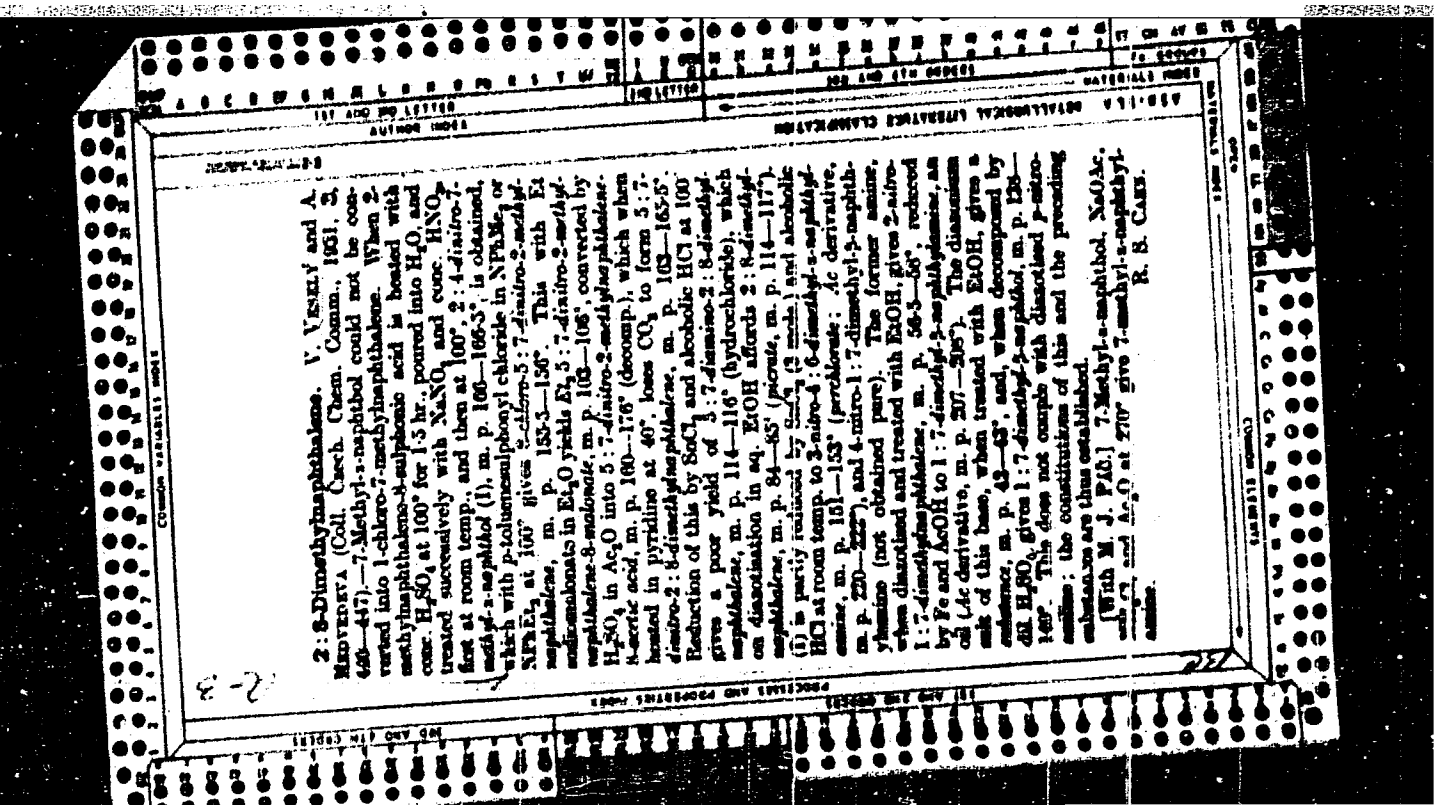
DC

a-3

[illegible] gadoleic and [illegible] acids. V. [illegible] and L. K. [illegible] (J. Gen. Chem. [illegible] 1937, 7, [illegible]—107).—[illegible] is reduced to [illegible] alcohol, which is converted into the bromide, and this latter is condensed with ethyl [illegible], and the dibasic acid so obtained loses carbon dioxide on distillation, yielding, together with the [illegible], a small quantity of [illegible]docosenoic acid identical with gadoleic acid (cf. Bull, A., 1906, I, 635). An identical synthetic process employing elaidic acid yields trans-docosenoic acid identical with gadelaidic acid, m. p. 53—54° (amide, m. p. 90—91°), obtained by the isomerising action of nitrous acid on gadoleic acid. Gadoleic and gadelaidic acids are, therefore, formulated as the cis- and trans-forms of the acid $CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_9\cdot CO_2H$. In the final stage of the synthesis, during the distillation, a degradation product, ()-hentriacontadiene, m. p. 48—49°, is formed which can be isolated from the higher fractions. Similarly, from erucic acid, by way of erucyl alcohol and erucyl bromide, b. p. 232—236°/10 mm., [illegible]tetracosenoic acid, m. p. 44—45° (amide, m. p. 87—88°), identical with Tsujimoto's selacholeic acid (B., 1926, 712), and from brassidic acid through brassidyl alcohol, m. p. 53—54°, b. p. 239—242°, and brassidyl bromide, m. p. 35—36°, b. p. 246—248°, trans-tetracosenoic acid (amide, m. p. [illegible]—99°), probably identical with selacholeidic acid (loc. cit.), have been obtained. The degradation product obtained in this synthesis from the higher fractions is ()-tetratriacontadiene, $C_{34}H_{66}$, m. p. 60—62°.

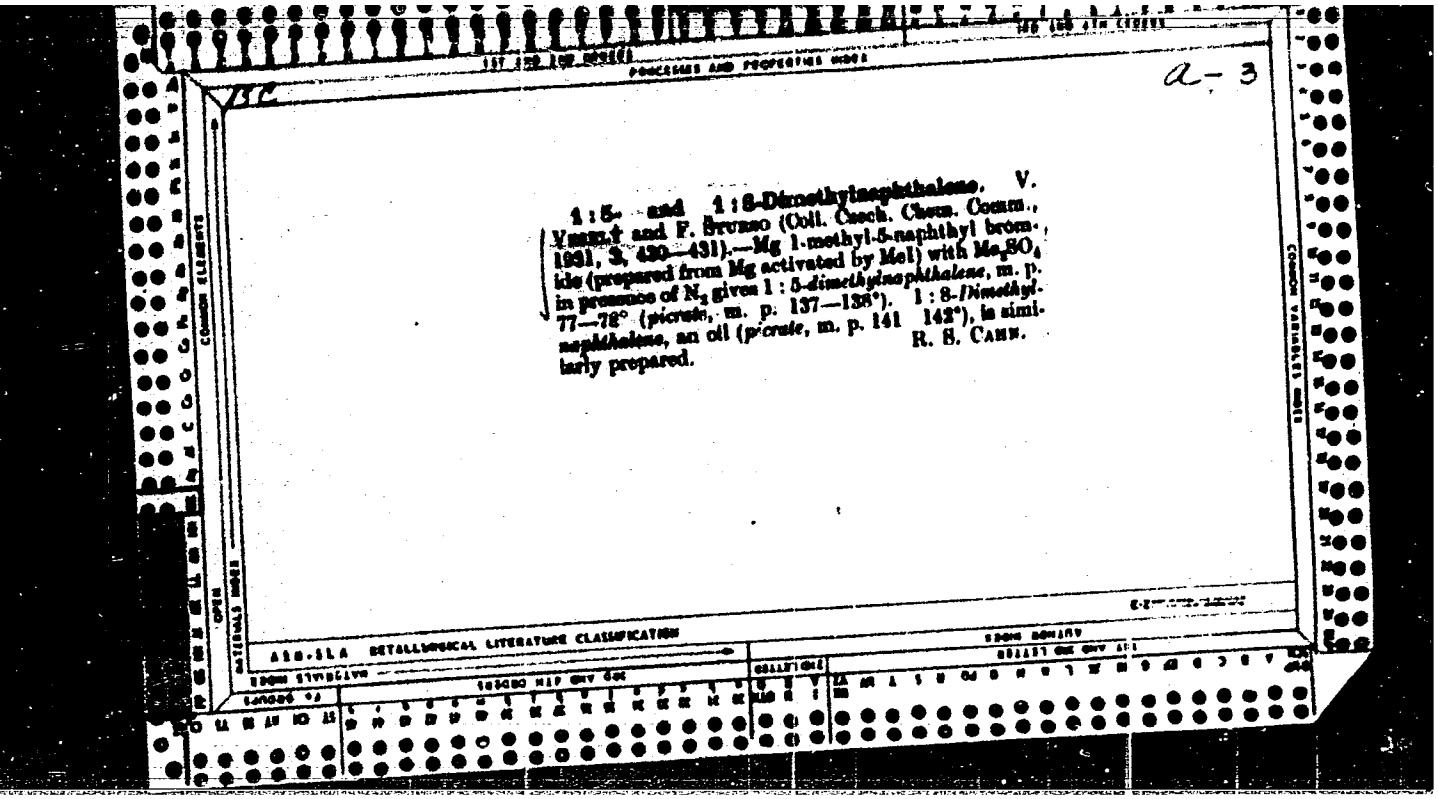
T. H. Morton.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



2 : 8-Dimethylnaphthalene. V. Vesely and A. Mentzerova (Coll. Czech. Chem. Comm., 1951, 16, 440—447).—7-Methyl-2-naphthol could not be converted into 1-chloro-7-methylnaphthalene. When 2-methylnaphthalene-4-sulphonic acid is heated with conc. H_2SO_4 at 100° for 1·5 hr., poured into H_2O, and treated successively with $NaNO_2$ and conc. HNO_3 at room temp., and then at 100°, 2 : 4-*dinitro*-7-*methyl*-2-*naphthol* (I), m. p. 100—105·5°, is obtained, which with *p*-toluenesulphonyl chloride in $NPhMe_2$ or $NPhEt_2$ at 100° gives 2-*chloro*-5 : 7-*dinitro*-2-*methyl*-*naphthalene*, m. p. 153·5—156°. This with Et mercaptoacetate in Et_2O yields Et_2 5 : 7-*dinitro*-2-*methyl*-*naphthalene*-8-*malonate*, m. p. 102—106°, converted by H_2SO_4 in Ac_2O into 5 : 7-*dinitro*-2-*methylnaphthalene*-8-*acetic acid*, m. p. 160—176° (decomp.), which when heated in pyridine at 40°, loses CO_2 to form 5 : 7-*dinitro*-2 : 8-*dimethylnaphthalene*, m. p. 102—165·5°. Reduction of this by $SnCl_2$ and alcoholic HCl at 100° gives a poor yield of 5 : 7-*diamino*-2 : 8-*dimethylnaphthalene*, m. p. 114—116° (hydrochloride), which on diazotisation in 84% EtOH affords 2 : 8-*dimethylnaphthalene*, m. p. 84—85° (*picrate*, m. p. 114—117°). (I) is partly reduced by $SnCl_2$ (2 mols.) and alcoholic HCl at room temp. to 3-*nitro*-4 : 6-*dimethyl*-2-*naphthylamine*, m. p. 151—153° (*perchlorate*: *Ac derivative*, m. p. 220—222°), and 4-*nitro*-1 : 7-*dimethyl*-2-*naphthylamine* (not obtained pure). The former amine, when diazotised and treated with EtOH, gives 2-*nitro*-1 : 7-*dimethylnaphthalene*, m. p. 56·5—58°, reduced by Fe and AcOH to 1 : 7-*dimethyl*-2-*naphthylamine*, as *Ac derivative*, m. p. 207—208°). The diazonium salt of this base, when treated with EtOH, gives a reference, m. p. 43—45°, and, when decomposed by dil H_2SO_4, gives 1 : 7-*dimethyl*-2-*naphthol*, m. p. 154—160°. This does not couple with diazotised *p*-nitroaniline; the constitution of this and the preceding substances are thus established.

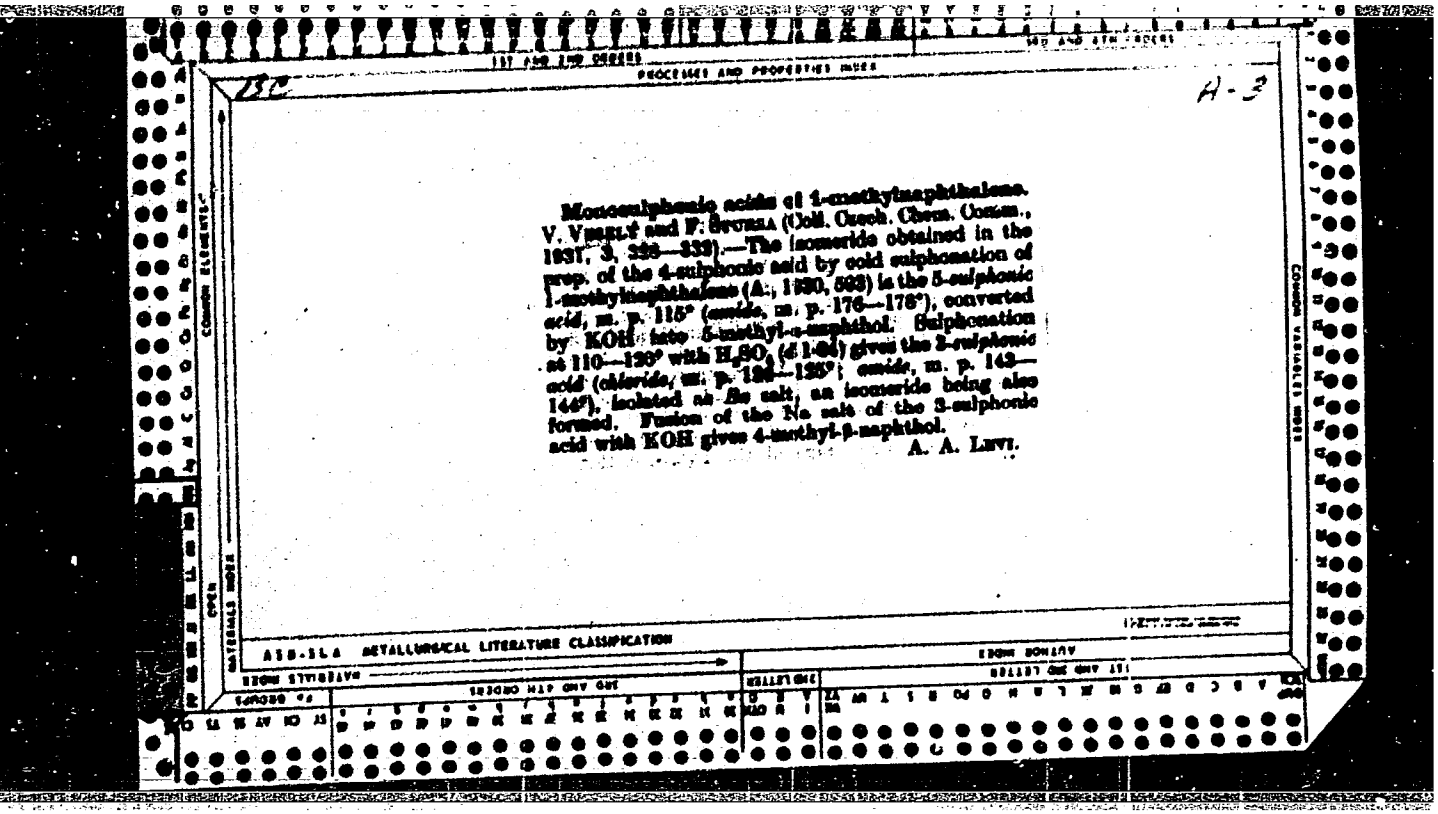
[With M. J. Pál.] 7-Methyl-2-naphthol, NaO_2Ac, and Ac_2O at 270° give 7-methyl-2-naphthyl-R. S. Cass.



a-3

1 : 5- and 1 : 8-Dimethylnaphthalene. V. Vesely and F. Bruzno (Coll. Czech. Chem. Commun., 1931, 3, 430—431).—Mg 1-methyl-5-naphthyl bromide (prepared from Mg activated by MeI) with Me_2SO_4 in presence of N_2 gives 1 : 5-*dimethylnaphthalene*, m. p. 77—78° (*picrate*, m. p. 137—138°). 1 : 8-*Dimethylnaphthalene*, an oil (*picrate*, m. p. 141—142°), is similarly prepared.

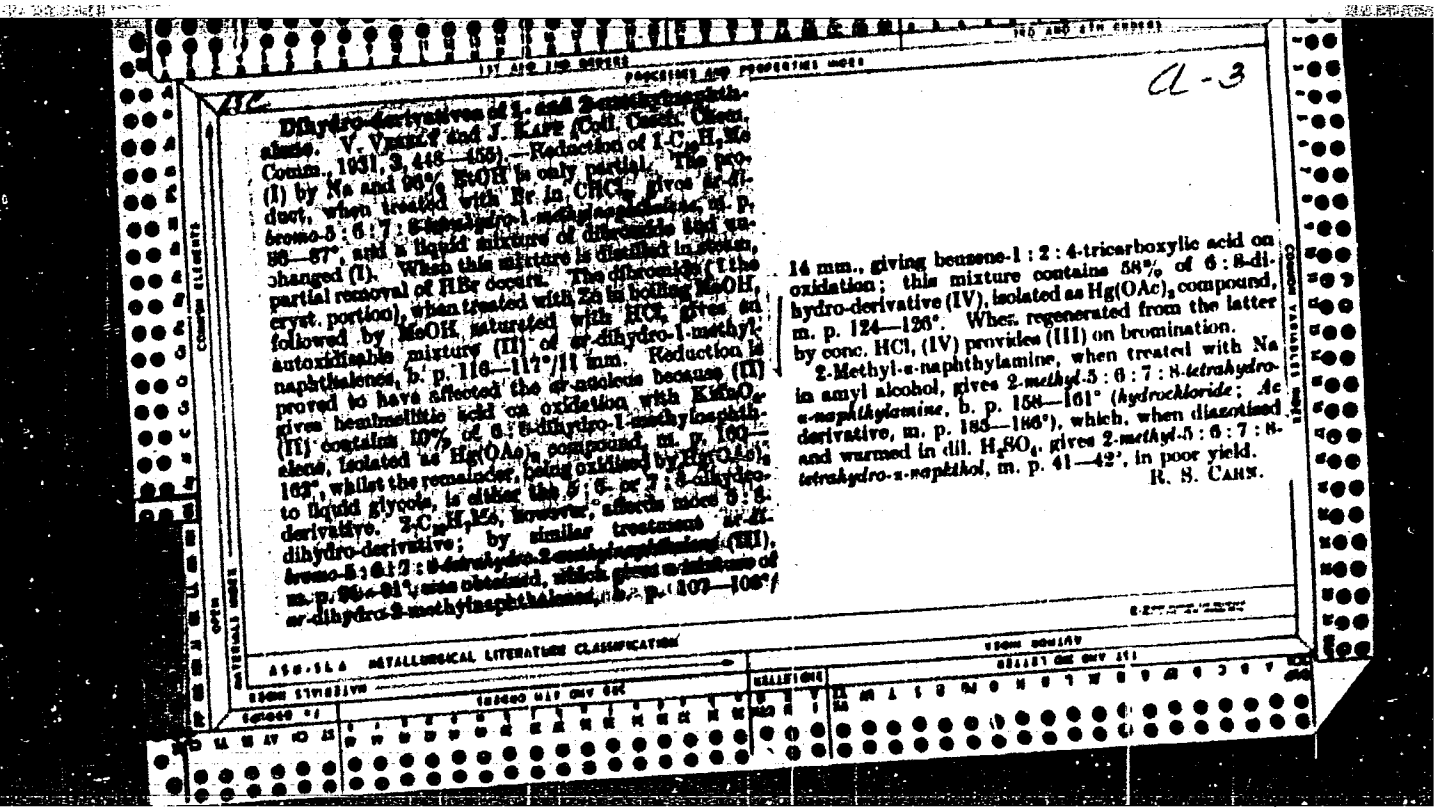
R. S. Cahn.



A-3

Monosulphonic acids of 1-methylnaphthalene. V. Vesely and F. Švrcina (Coll. Czech. Chem. Comm., 1931, 3, 326—339).—The isomeride obtained in the prep. of the 4-sulphonic acid by cold sulphonation of 1-methylnaphthalene (A., 1930, 503) is the *5-sulphonic acid*, m. p. 115° (*amide*, m. p. 176—178°), converted by KOH into 5-methyl-α-naphthol. Sulphonation at 110—120° with H_2SO_4 (d 1·84) gives the *3-sulphonic acid* (*chloride*, m. p. 128—130°; *amide*, m. p. 142—144°), isolated as Na salt, an isomeride being also formed. Fusion of the Na salt of the 3-sulphonic acid with KOH gives 4-methyl-β-naphthol.

A. A. Levi.



A-3

Dihydro-derivatives of 1- and 2-methylnaphthalene. V. Vesely and J. Kaye (Coll. Czech. Chem. Comm., 1931, 3, 448—455).—Reduction of 1-$C_{10}H_7Me$ (I) by Na and 96% EtOH is only partial. The product, when treated with Br in $CHCl_3$, gives 5:6:7:8-tetrabromo-1-methylnaphthalene, m. p. 86—87°, and a liquid mixture of dibromides that unchanged (I). When this mixture is distilled in steam, partial removal of HBr occurs. The dibromide (the cryst. portion), when treated with Zn in boiling MeOH, followed by MeOH saturated with HCl, gives an autoxidisable mixture (II) of 5:6-dihydro-1-methylnaphthalene, b. p. 116—117°/11 mm. Reduction is proved to have affected the *o*-nucleus because (II) gives hemimellitic acid on oxidation with $KMnO_4$. (II) contains 10% of 5:8-dihydro-1-methylnaphthalene, isolated as $Hg(OAc)_2$ compound, m. p. 160—162°, whilst the remainder, being oxidised by $Hg(OAc)_2$ to liquid glycols, is either the 5:6- or 7:8-dihydro-derivative. 2-$C_{10}H_7Me$, however, affords mixed 5:8-dihydro-derivative; by similar treatment 5:6:7:8-tetrabromo-2-methylnaphthalene (III), m. p. 96—97°, was obtained, which gives a mixture of 5:6- and 7:8-dihydro-2-methylnaphthalene, b. p. 107—108°/14 mm., giving benzene-1:2:4-tricarboxylic acid on oxidation; this mixture contains 58% of 6:8-dihydro-derivative (IV), isolated as $Hg(OAc)_2$ compound, m. p. 124—126°. When regenerated from the latter by conc. HCl, (IV) provides (III) on bromination.

2-Methyl-α-naphthylamine, when treated with Na in amyl alcohol, gives 2-*methyl*-5:6:7:8-*tetrahydro*-α-*naphthylamine*, b. p. 158—161° (*hydrochloride*; *Ac derivative*, m. p. 183—186°), which, when diazotised and warmed in dil. H_2SO_4, gives 2-*methyl*-5:6:7:8-*tetrahydro*-α-*naphthol*, m. p. 41—42°, in poor yield.

R. S. Cahn.

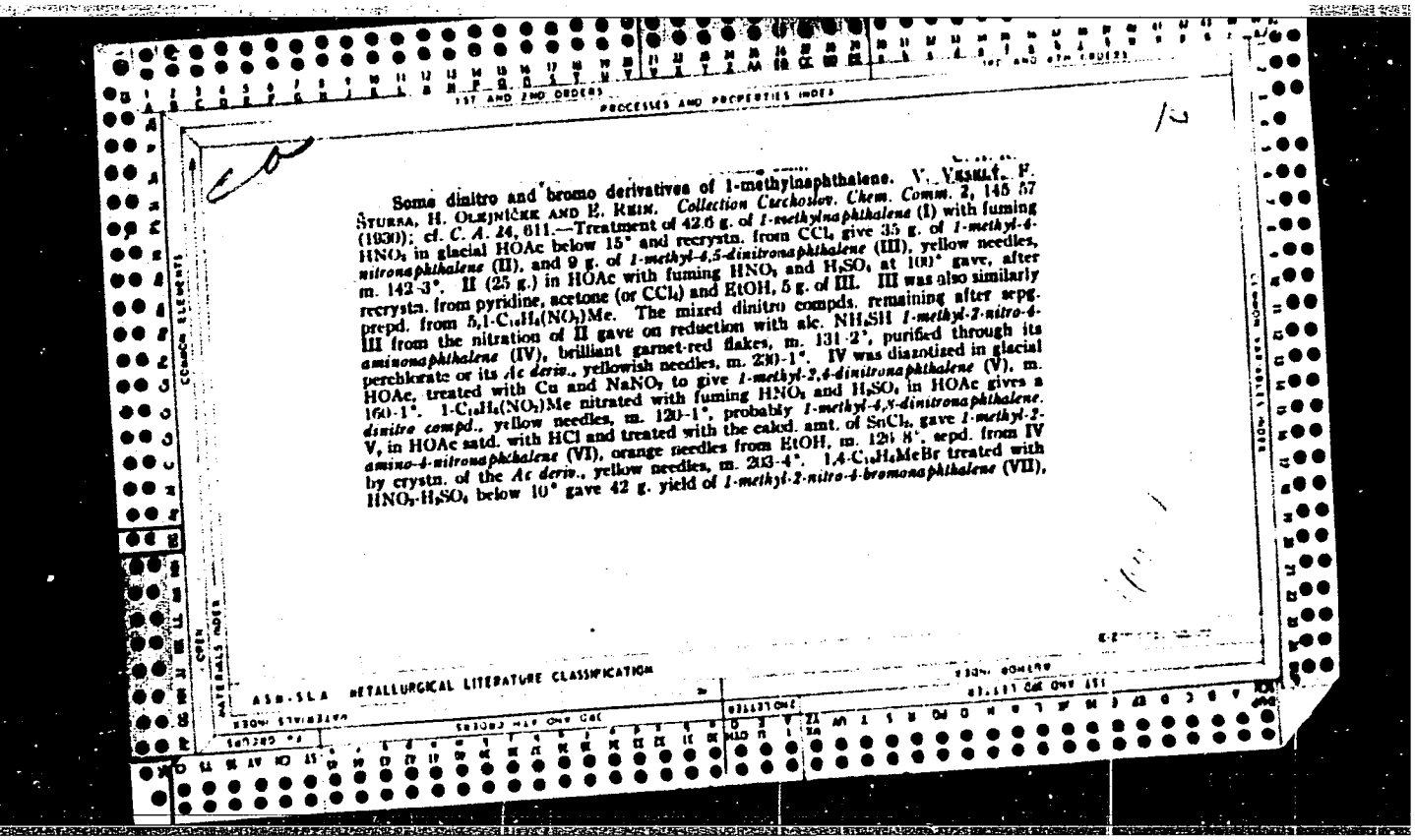
1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

A-3

Use of lithium for synthesis of naphthalene homologues. V. VESELÝ and F. ŠTURSA (Coll. Czech. Chem. Comm., 1932, 4, 139—144).—Methylnaphthalenes are obtained by the action of Me_2SO_4 on the Li compound obtained from 1-halogenonaphthalenes and Li in dry Et_2O in a N_2 atm.; diaryls also being formed. The yield of methylnaphthalenes decreases in the order X = Cl > Br > I, and with 2-halogenonaphthalenes diaryls are the sole products except when X = Cl. Reduction of 1-nitro-2-methylnaphthalene with $SnCl_2$ affords 4-chloro-2-methyl-α-naphthylamine, converted by diazotisation into 4-chloro-2-methylnaphthalene, b. p. 150—160°/16 mm. (picrate, m. p. 70—80°), similarly converted into 1 : 2-dimethylnaphthalene. J. W. BAKER.

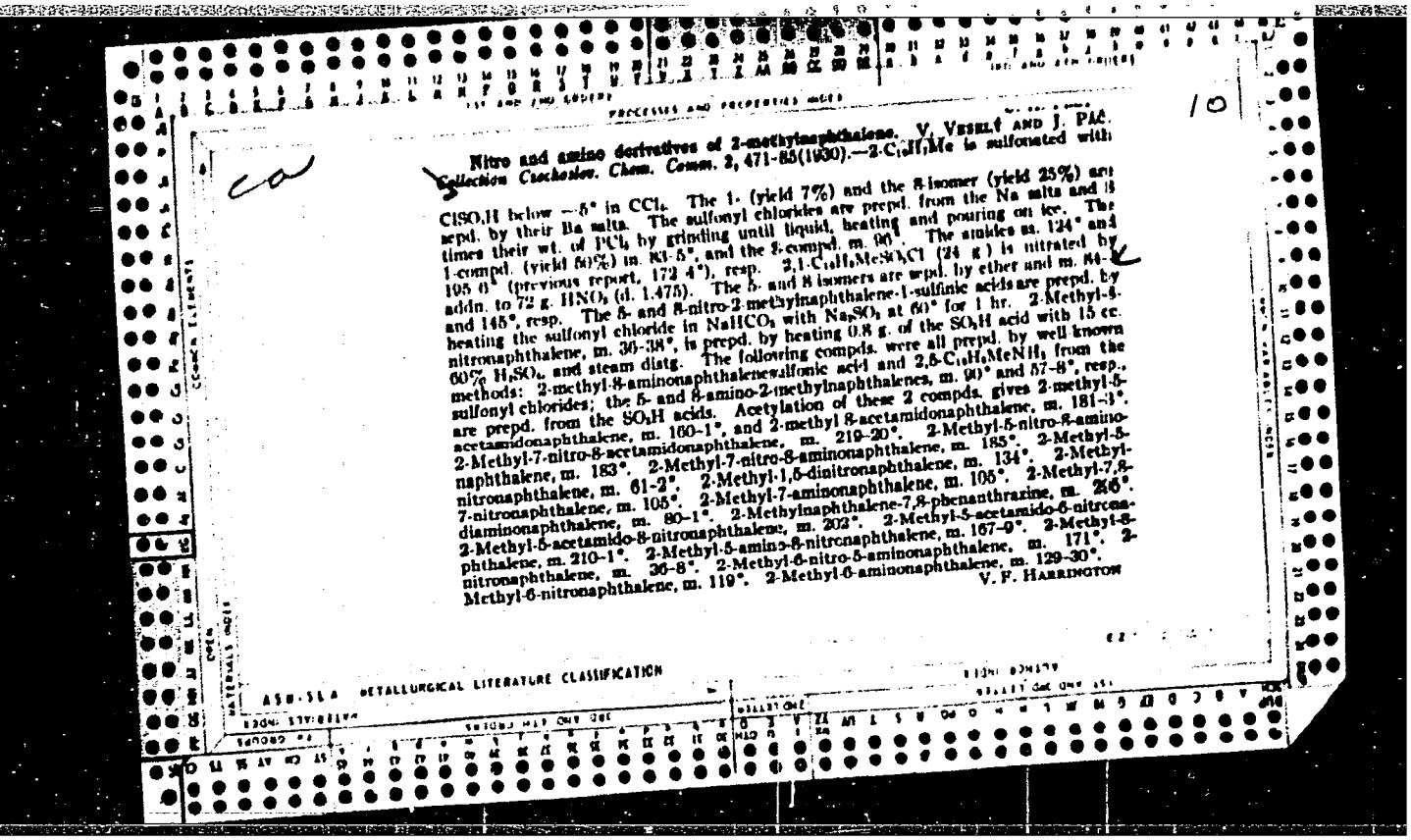
ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION



Some dinitro and bromo derivatives of 1-methylnaphthalene. V. Vesely, F. Sturba, H. Olejníček and E. Rein. *Collection Czechoslov. Chem. Comm.* 2, 145-57 (1930); cf. *C. A.* 24, 611.—Treatment of 42.6 g. of *1-methylnaphthalene* (I) with fuming HNO_3 in glacial HOAc below 15° and recrystn. from CCl_4 give 35 g. of *1-methyl-4-nitronaphthalene* (II), and 9 g. of *1-methyl-4,5-dinitronaphthalene* (III), yellow needles, m. 142-3°. II (25 g.) in HOAc with fuming HNO_3 and H_2SO_4 at 10° gave, after recrystn. from pyridine, acetone (or CCl_4) and EtOH, 5 g. of III. III was also similarly prepd. from 5,1-$C_{10}H_6(NO_2)Me$. The mixed dinitro compds. remaining after sepn. of III from the nitration of II gave on reduction with alc. NH_4SH *1-methyl-2-nitro-4-aminonaphthalene* (IV), brilliant garnet-red flakes, m. 131-2°, purified through its perchlorate or its *Ac deriv.*, yellowish needles, m. 238-1°. IV was diazotized in glacial HOAc, treated with Cu and $NaNO_2$ to give *1-methyl-2,4-dinitronaphthalene* (V), m. 160-1°. 1-$C_{10}H_6(NO_2)Me$ nitrated with fuming HNO_3 and H_2SO_4 in HOAc gives a *dinitro compd.*, yellow needles, m. 120-1°, probably *1-methyl-4,8-dinitronaphthalene*. V, in HOAc satd. with HCl and treated with the calcd. amt. of $SnCl_2$, gave *1-methyl-2-amino-4-nitronaphthalene* (VI), orange needles from EtOH, m. 203-4°. 1,4-$C_{10}H_6MeBr$ treated with HNO_3-H_2SO_4 below 10° gave 42 g. yield of *1-methyl-2-nitro-4-bromonaphthalene* (VII),

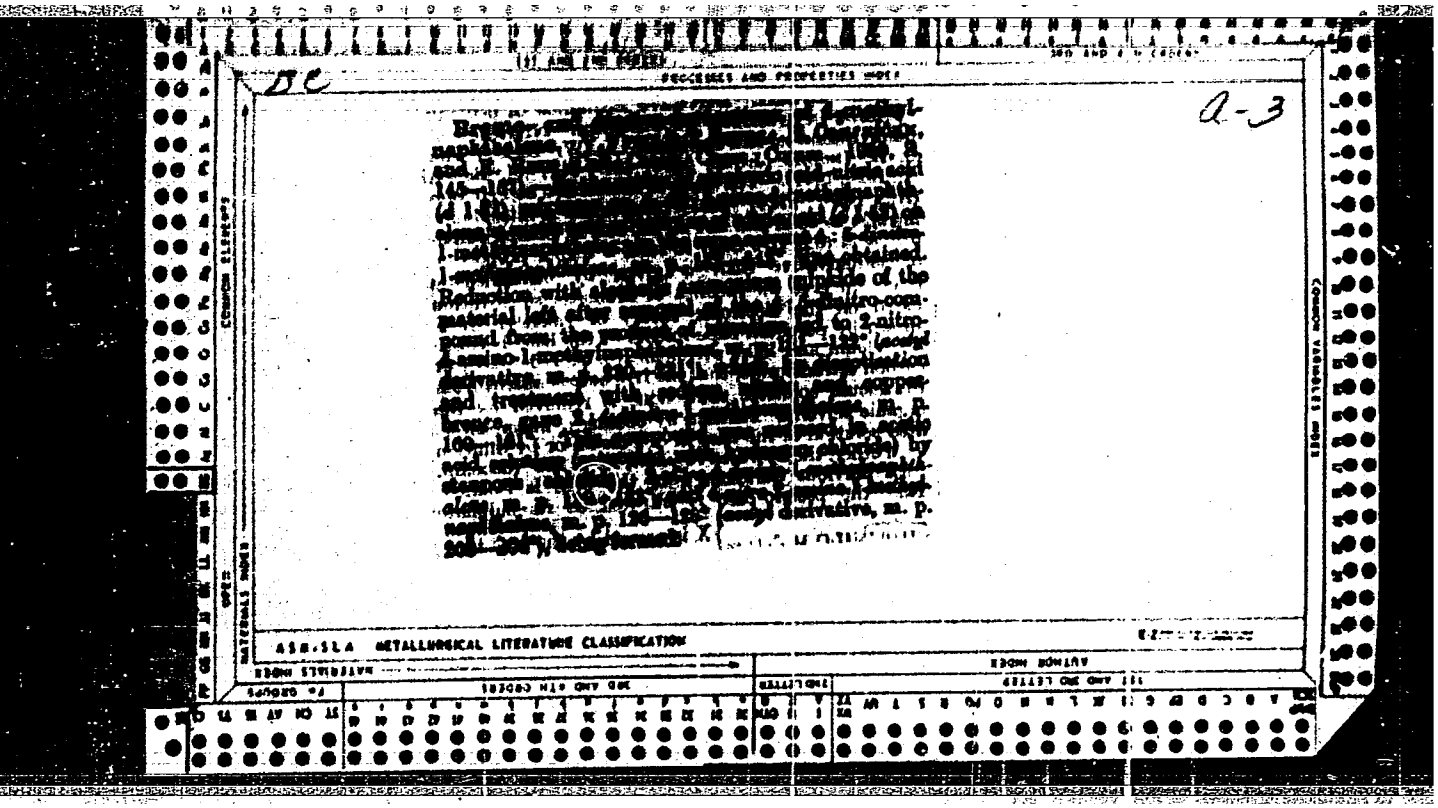
long yellow needles from EtOH, m. 121–2°. Reduction of 2 g. of VII with $SnCl_2$ gave 1.2 g. of *1-methyl-2-amino-4-bromonaphthalene* (VIII), pearly plates from EtOH, m. 78°; *Ac deriv.*, m. 224.4°. VIII was diazotized, decompd. with H_2SO_4 to give *1-methyl-2-hydroxy-4-bromonaphthalene*, m. 108.0°. VIII, diazotized and treated with CuBr, gave *1-methyl-2,4-dibromonaphthalene* (IX), m. 58.0°. II (25 g.) treated with Br, gave 12 g. pure *1-methyl-2-bromo-4-nitronaphthalene* (X), yellow needles from EtOH, m. 138.9°; when $FeBr_3$ is used as catalyst there are obtained other brominated derivs.: *mono-Br deriv.*, m. 120°, one of unknown compn., m. 158° and a *di-Br deriv.*, m. 210°. Ten g. of X on reduction with $SnCl_2$ gave 4.1 g. *1-methyl-2-bromo-4-aminonaphthalene* (XI), m. 118.0°; *Ac deriv.*, m. 206–7°. Replacement of Br for NH_2 in XI gave IX. XI was diazotized and decompd. with alc. to give *1-methyl-2-bromonaphthalene* (XII), yellow plates from petroleum ether, m. 35.0°; *picrate*, orange-yellow needles, m. 105.6°. XII was prepd. also from 2,1-$C_{10}H_6(NH_2)Me$. II diazotized and decompd. with H_2SO_4 gave *1-methyl-2-bromo-4-hydroxynaphthalene*, m. 128.9°, which was oxidized with alk. $KMnO_4$ to phthalic acid. *1-Methyl-3-bromonaphthalene*, m. 63–4°, *picrate*, m. orange-yellow needles, m. 83–4°; *1-methyl-5-bromonaphthalene*, pearly plates from EtOH, m. 80°, *picrate*, 110–1°; and *1-methyl-8-bromonaphthalene*, pearly plates from EtOH, m. 80°, *picrate*, m. 152–3°, were prepd. from the corresponding amines by the Sandmeyer reaction.

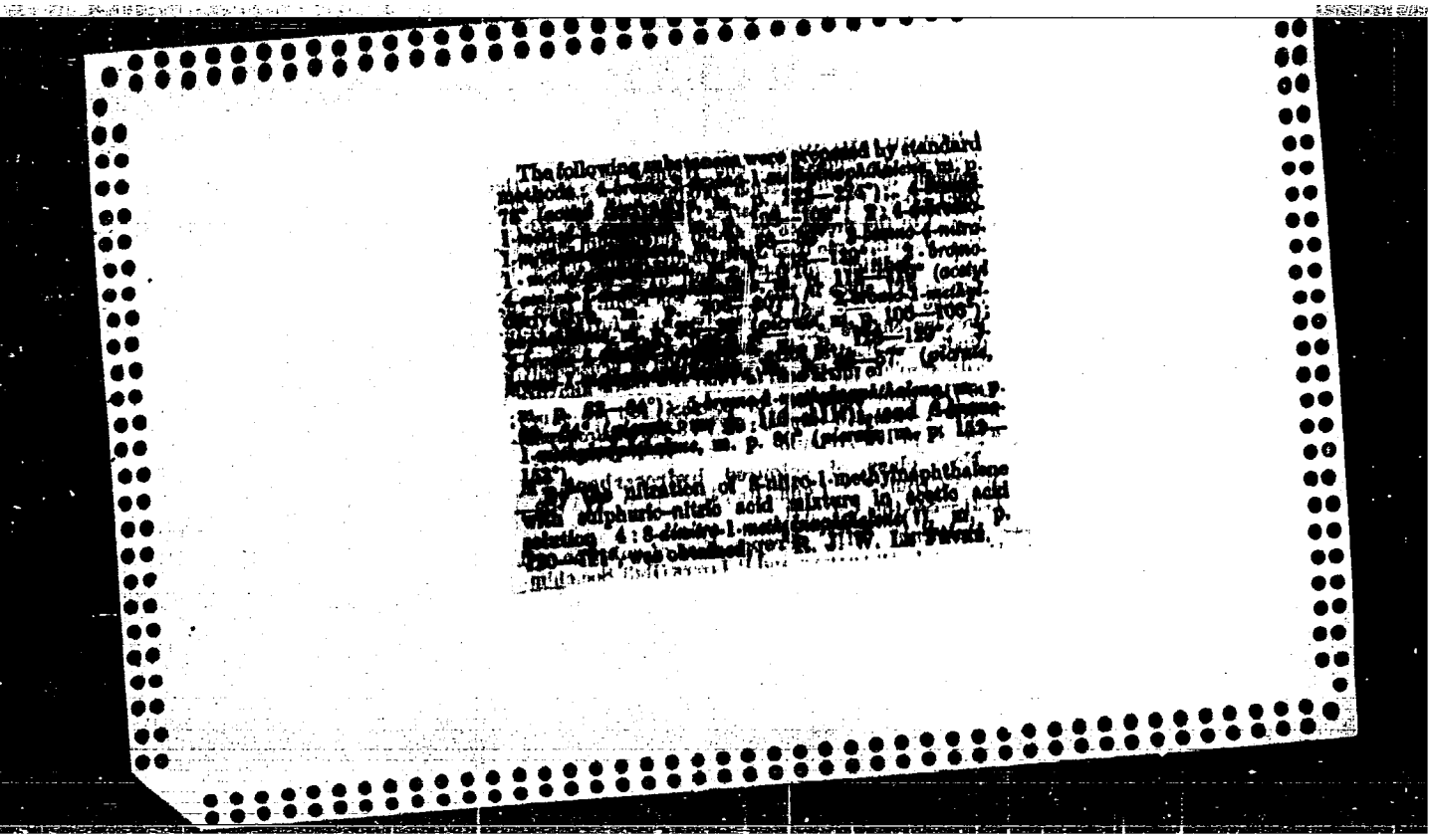
G. R. YOHE.

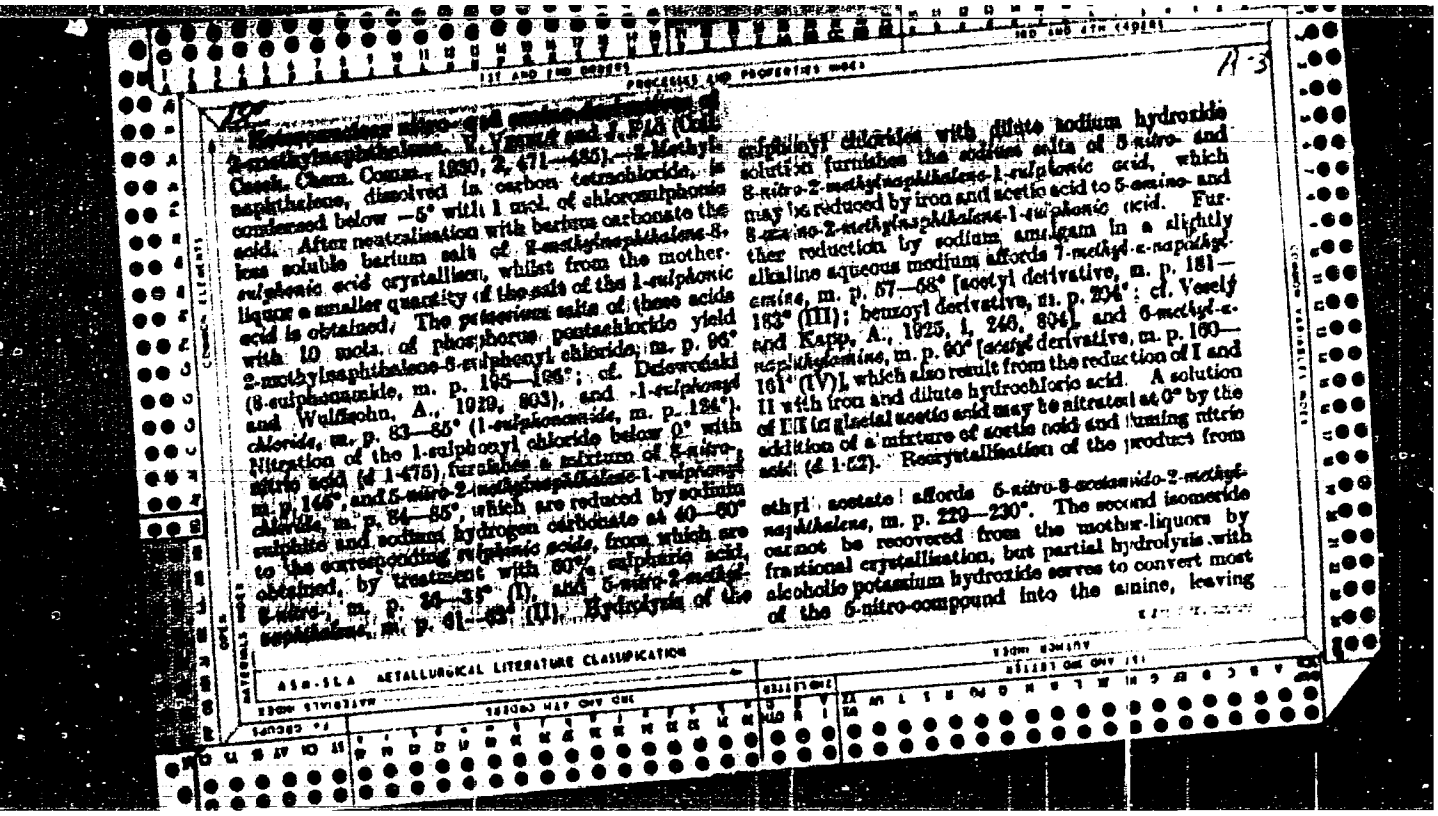


Nitro and amino derivatives of 2-methylnaphthalene. V. Veselý and J. Pác. *Collection Czechoslov. Chem. Comm.* 2, 471-85(1930).—2-$C_{10}H_7Me$ is sulfonated with ClSO$_3$H below −5° in CCl_4. The 1- (yield 7%) and the 8-isomer (yield 25%) are sepd. by their Ba salts. The sulfonyl chlorides are prepd. from the Na salts and 3 times their wt. of PCl_5 by grinding until liquid, heating and pouring on ice. The 1-compd. (yield 60%) m. 83-5°, and the 8-compd. m. 90°. The amides m. 124° and 195.5° (previous report, 172.4°), resp. 2,1-$C_{10}H_6MeSO_2Cl$ (24 g.) is nitrated by addn. to 72 g. HNO_3 (d. 1.475). The 5- and 8 isomers are sepd. by ether and m. 84- and 145°, resp. The 5- and 8-nitro-2-methylnaphthalene-1-sulfinic acids are prepd. by heating the sulfonyl chloride in $NaHCO_3$ with Na_2SO_3 at 60° for 1 hr. 2-Methyl-5-nitronaphthalene, m. 36-38°, is prepd. by heating 0.8 g. of the SO_2H acid with 15 cc. 60% H_2SO_4 and steam distg. The following compds. were all prepd. by well known methods: 2-methyl-8-aminonaphthalenesulfonic acid and 2,5-$C_{10}H_5MeNH_2$ from the sulfonyl chlorides; the 5- and 8-amino-2-methylnaphthalenes, m. 90° and 57-8°, resp., are prepd. from the SO_2H acids. Acetylation of these 2 compds. gives 2-methyl-5-acetamidonaphthalene, m. 160-1°, and 2-methyl 8-acetamidonaphthalene, m. 219-20°. 2-Methyl-5-nitro-8-amino-2-Methyl-7-nitro-8-acetamidonaphthalene, m. 185°. 2-Methyl-5-naphthalene, m. 183°. 2-Methyl-7-nitro-8-aminonaphthalene, m. 134°. 2-Methyl-nitronaphthalene, m. 61-2°. 2-Methyl-1,5-dinitronaphthalene, m. 105°. 2-Methyl-7,8-7-nitronaphthalene, m. 105°. 2-Methyl-7-aminonaphthalene, m. 206°. diaminonaphthalene, m. 80-1°. 2-Methylnaphthalene-7,8-phenanthrazine, m. 2-Methyl-5-acetamido-8-nitronaphthalene, m. 202°. 2-Methyl-5-acetamido-6-nitronaphthalene, m. 210-1°. 2-Methyl-5-amino-8-nitronaphthalene, m. 167-9°. 2-Methyl-8-nitronaphthalene, m. 36-8°. 2-Methyl-6-nitro-5-aminonaphthalene, m. 129-30°. Methyl-6-nitronaphthalene, m. 119°. 2-Methyl-6-aminonaphthalene, m. 171°. 2-

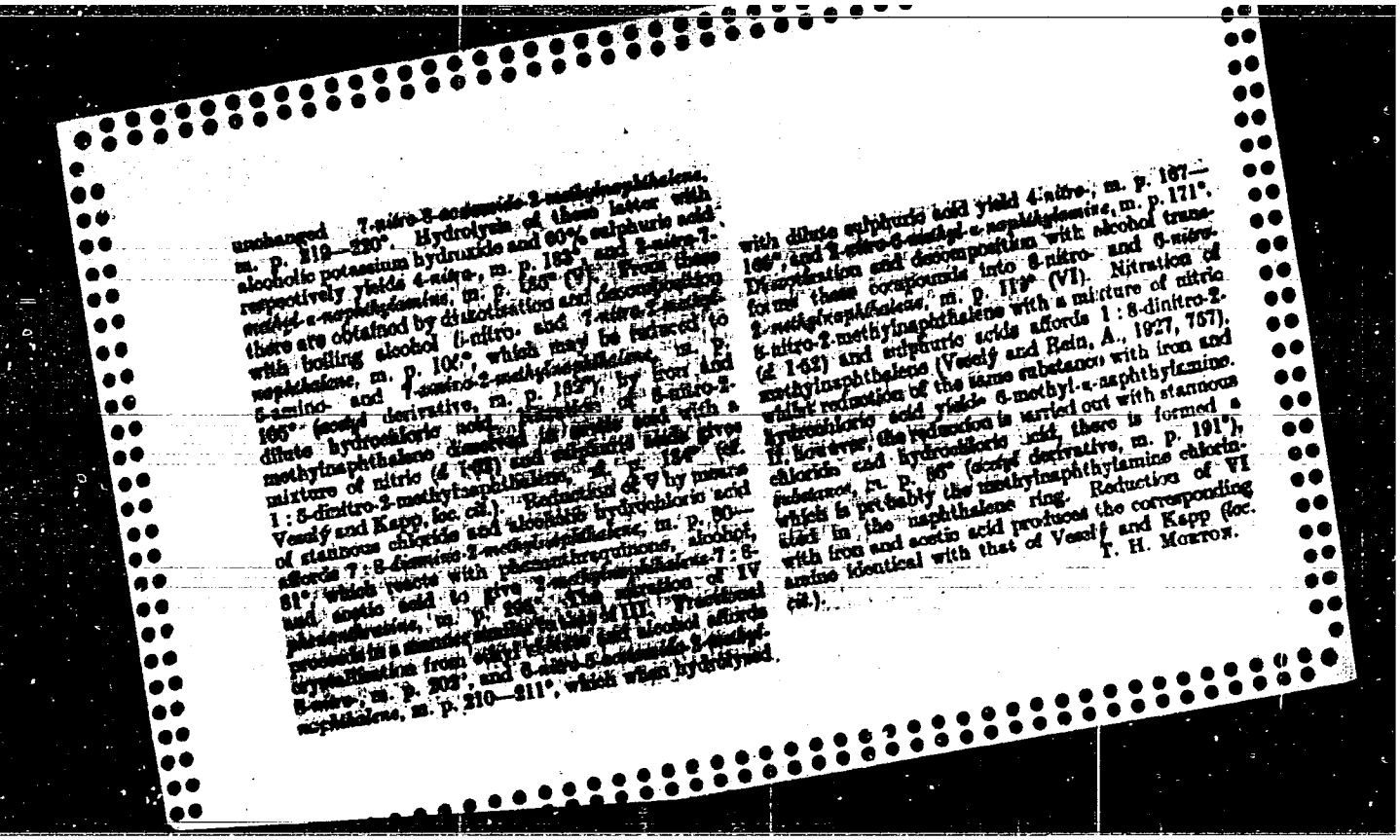
V. F. Harrington





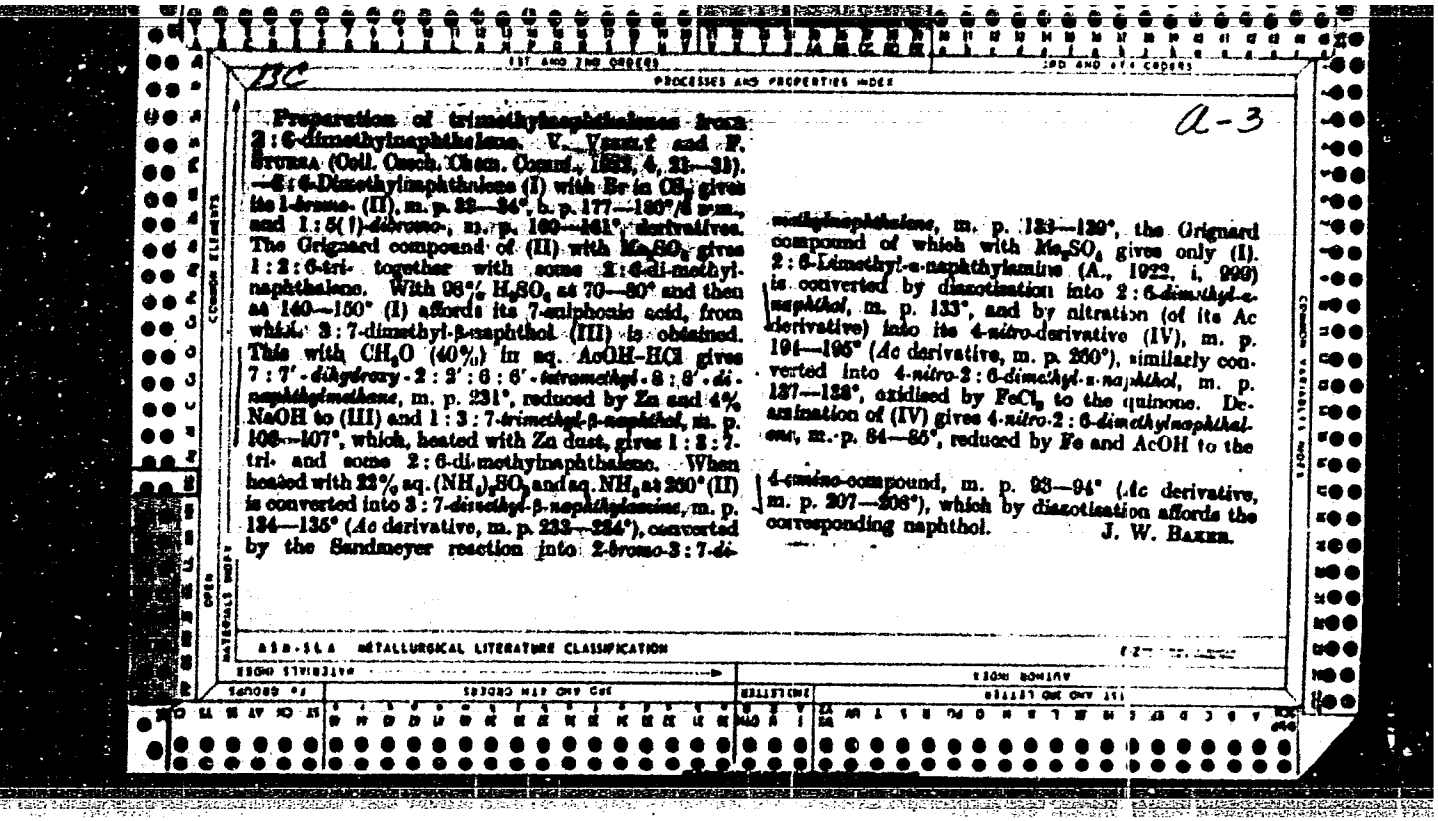


sulphonyl chlorides with dilute sodium hydroxide solution furnishes the sodium salts of 5-*nitro*- and 8-*nitro*-2-*methylnaphthalene*-1-*sulphonic acid*, which may be reduced by iron and acetic acid to 5-*amino*- and 8-*amino*-2-*methylnaphthalene*-1-*sulphonic acid*. Further reduction by sodium amalgam in a slightly alkaline aqueous medium affords 7-*methyl*-α-*naphthylamine*, m. p. 57—58° [*acetyl* derivative, m. p. 181—183° (III); *benzoyl* derivative, m. p. 204°; cf. Veselý and Kapp, A., 1925, I, 246, 804], and 6-*methyl*-α-*naphthylamine*, m. p. 60° [*acetyl* derivative, m. p. 160—161° (IV)], which also result from the reduction of I and II with iron and dilute hydrochloric acid. A solution of III in glacial acetic acid may be nitrated at 0° by the addition of a mixture of acetic acid and fuming nitric acid (*d* 1·52). Recrystallisation of the product from ethyl acetate affords 5-*nitro*-8-*acetamido*-2-*methylnaphthalene*, m. p. 229—230°. The second isomeride cannot be recovered from the mother-liquors by fractional crystallisation, but partial hydrolysis with alcoholic potassium hydroxide serves to convert most of the 5-nitro-compound into the amine, leaving



unchanged 7-*nitro*-8-*acetamido*-2-*methylnaphthalene*, m. p. 219—220°. Hydrolysis of these latter with alcoholic potassium hydroxide and 60% sulphuric acid respectively yields 4-*nitro*-, m. p. 183°, and 8-*nitro*-7-*methyl*-α-*naphthylamine*, m. p. 185° (?). From these there are obtained by diazotisation and decomposition with boiling alcohol (*i*-nitro- and 7-*nitro*-2-*methyl*-naphthalene, m. p. 104°, which may be reduced to 5-*amino*- and 7-*amino*-2-*methylnaphthalene*, m. p. 165° (acetyl derivative, m. p. 182°), by iron and dilute hydrochloric acid, respectively. 5-*Nitro*-2-methylnaphthalene dissolved in acetic acid with a mixture of nitric (*d* 1·42) and sulphuric acids gives 1 : 5-*dinitro*-2-*methylnaphthalene*, m. p. 154° (cf. Vesely and Kapp, *loc. cit.*). Reduction of V by means of stannous chloride and alcoholic hydrochloric acid affords 7 : 8-*diamino*-2-*methylnaphthalene*, m. p. 80—81°, which reacts with phenanthraquinone, alcohol, and acetic acid to give 2-*methylnaphthaphenazine*, m. p. 205°. The nitration of IV proceeds in a manner similar to that of VIII. Fractional crystallisation from ethyl acetate and alcohol affords 8-*nitro*-, m. p. 202°, and 6-*nitro*-8-*acetamido*-2-*methylnaphthalene*, m. p. 210—211°, which when hydrolysed with dilute sulphuric acid yield 4-*nitro*-, m. p. 187—188°, and 2-*nitro*-6-*methyl*-α-*naphthylamine*, m. p. 171°. Diazotisation and decomposition with alcohol transform these compounds into 8-*nitro*- and 6-*nitro*-2-*methylnaphthalene*, m. p. 113° (VI). Nitration of 6-*nitro*-2-methylnaphthalene with a mixture of nitric (*d* 1·42) and sulphuric acids affords 1 : 6-*dinitro*-2-methylnaphthalene (Vesely and Reiu, *A.*, 1927, 757). Whilst reduction of the same substance with iron and hydrochloric acid yields 6-*methyl*-α-*naphthylamine*. If, however, the reduction is carried out with stannous chloride and hydrochloric acid, there is formed a substance, m. p. 95° (acetyl derivative, m. p. 191°), which is probably the methylnaphthylamine chlorin-ated in the naphthalene ring. Reduction of VI with iron and acetic acid produces the corresponding amine identical with that of Vesely and Kapp (*loc. cit.*).

T. H. Morton.



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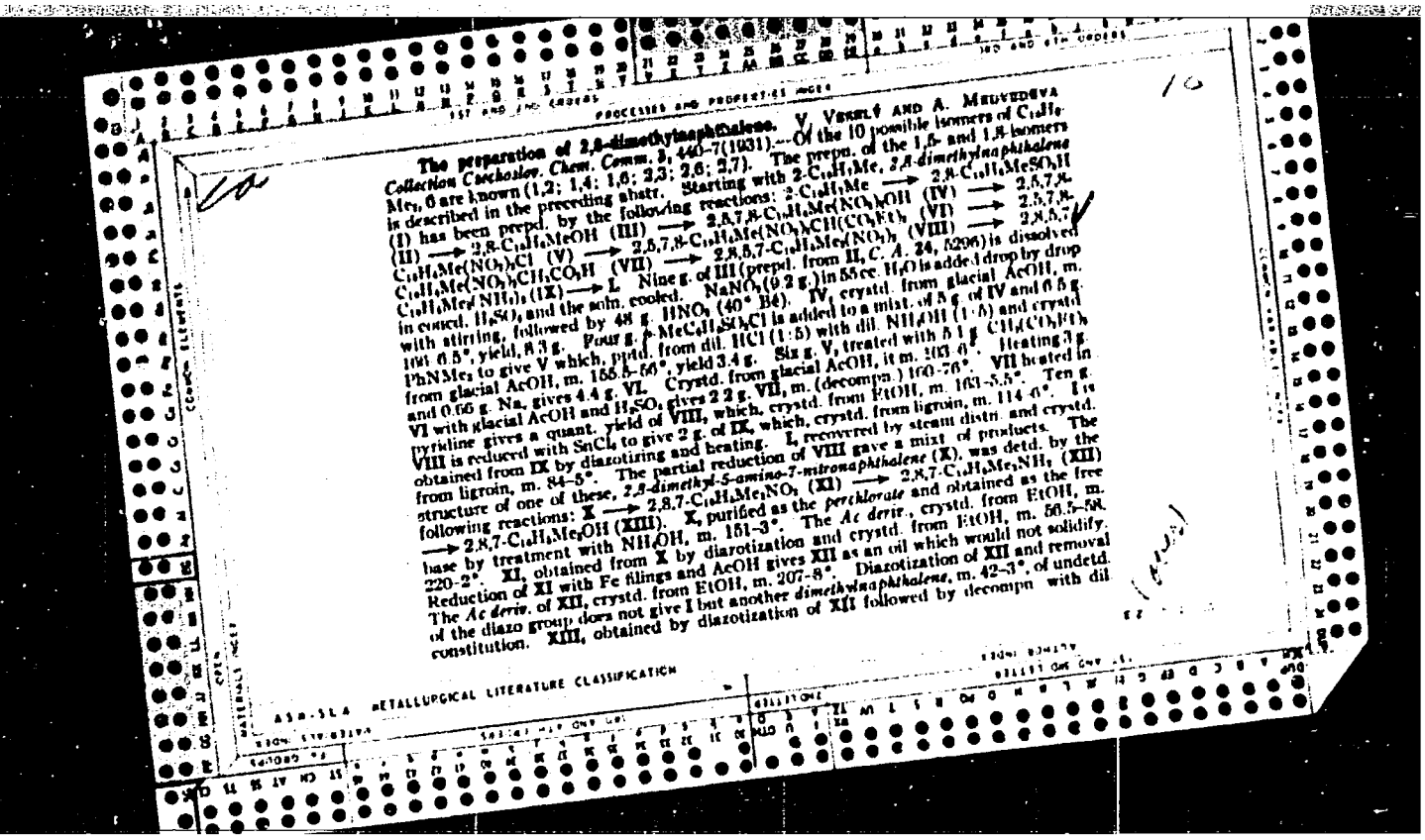
PROCESSES AND PROPERTIES INDEX

a-3

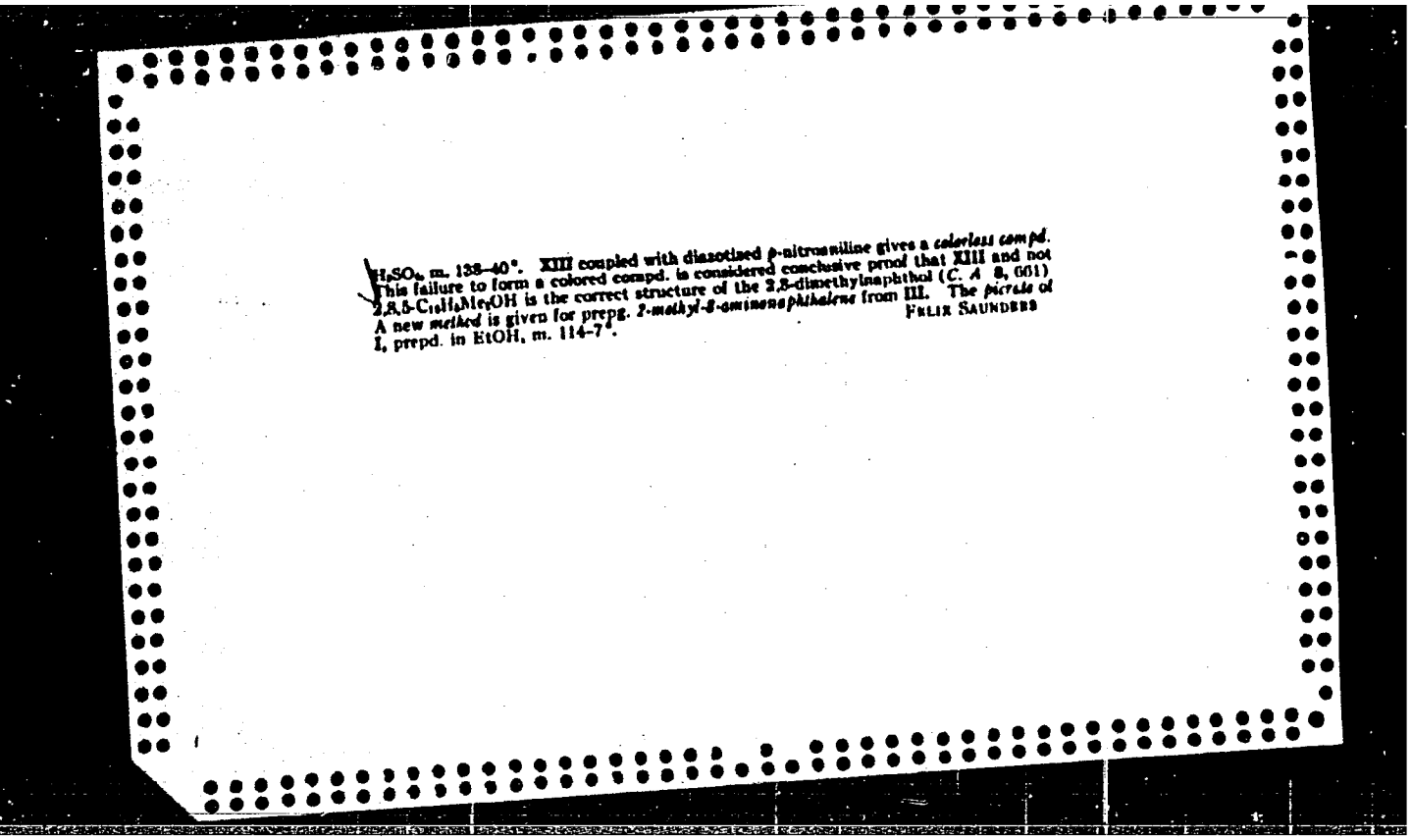
Preparation of trimethylnaphthalenes from 2 : 6-dimethylnaphthalene. V. Vesely and F. Sruska (Coll. Czech. Chem. Commun., 1932, 4, 21—31). —6 : 6-Dimethylnaphthalene (I) with Br in CS_2 gives its 1-bromo- (II), m. p. 33—34°, b. p. 177—180°/3 mm., and 1 : 5(?)-dibromo-, m. p. 160—161°, derivatives. The Grignard compound of (II) with Me_2SO_4 gives 1 : 2 : 6-tri- together with some 2 : 6-di-methyl-naphthalene. With 98% H_2SO_4 at 70—80° and then at 140—150° (I) affords its 7-sulphonic acid, from which 2 : 7-dimethyl-β-naphthol (III) is obtained. This with CH_2O (40%) in aq. AcOH–HCl gives 7 : 7'-*dihydroxy*-2 : 2' : 6 : 6'-*tetramethyl*-8 : 8'-*di-naphthylmethane*, m. p. 231°, reduced by Zn and 4% NaOH to (III) and 1 : 3 : 7-*trimethyl*-β-*naphthol*, m. p. 106—107°, which, heated with Zn dust, gives 1 : 3 : 7-tri- and some 2 : 6-di-methylnaphthalene. When heated with 22% aq. $(NH_4)_2SO_3$ and aq. NH_3 at 260° (II) is converted into 3 : 7-*dimethyl*-β-*naphthylamine*, m. p. 134—135° (*Ac* derivative, m. p. 233—234°), converted by the Sandmeyer reaction into 2-*bromo*-3 : 7-*dimethylnaphthalene*, m. p. 123—129°, the Grignard compound of which with Me_2SO_4 gives only (I). 2 : 6-*Dimethyl*-α-*naphthylamine* (A., 1922, i, 999) is converted by diazotisation into 2 : 6-*dimethyl*-α-*naphthol*, m. p. 133°, and by nitration (of its Ac derivative) into its 4-*nitro*-derivative (IV), m. p. 194—195° (*Ac* derivative, m. p. 260°), similarly converted into 4-*nitro*-2 : 6-*dimethyl*-α-*naphthol*, m. p. 137—138°, oxidised by $FeCl_3$ to the quinone. Deamination of (IV) gives 4-*nitro*-2 : 6-*dimethylnaphthalene*, m. p. 84—85°, reduced by Fe and AcOH to the 4-*amino*-compound, m. p. 93—94° (*Ac* derivative, m. p. 207—208°), which by diazotisation affords the corresponding naphthol.

J. W. Baker.

A.S.T.M. METALLURGICAL LITERATURE CLASSIFICATION

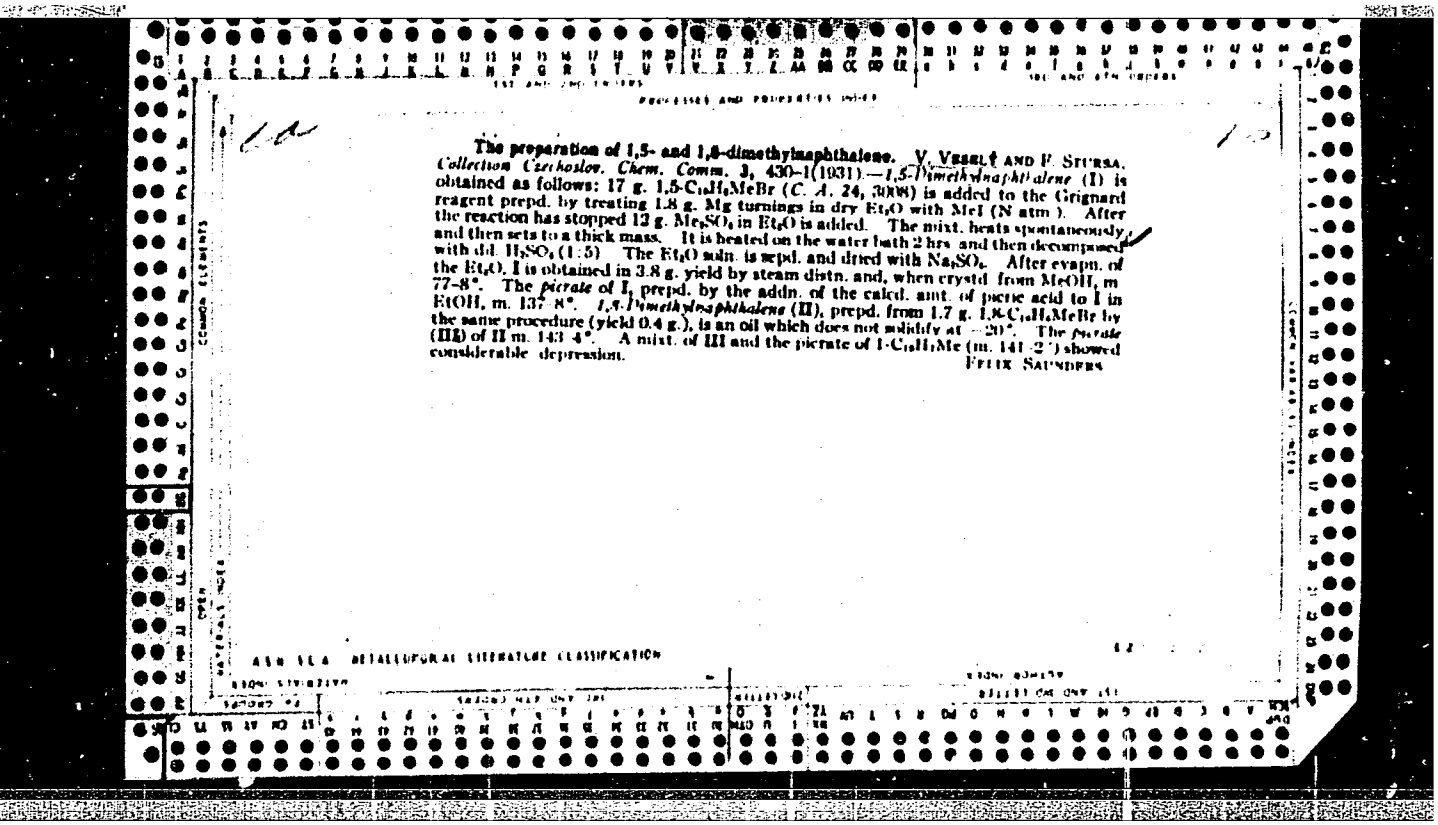


The preparation of 2,8-dimethylnaphthalene. V. Vesely and A. Medvedova *Collection Czechoslov. Chem. Comms.* 3, 440–7(1931).—Of the 10 possible isomers of $C_{12}H_6Me_2$, 6 are known (1,2; 1,4; 1,6; 2,3; 2,6; 2,7). The prepn. of the 1,6- and 1,8-isomers is described in the preceding abstr. Starting with 2-$C_{10}H_7Me$, *2,8-dimethylnaphthalene* (I) has been prepd. by the following reactions: 2-$C_{10}H_7Me \longrightarrow$ 2,8-$C_{10}H_6MeSO_3H$ (II) $\longrightarrow$ 2,8-$C_{10}H_6MeOH$ (III) $\longrightarrow$ 2,8,7,8-$C_{10}H_6Me(NO_2)OH$ (IV) $\longrightarrow$ 2,5,7,8-$C_{10}H_6Me(NO_2)Cl$ (V) $\longrightarrow$ 2,5,7,8-$C_{10}H_6Me(NO_2)CH_2CO_2H$ (VII) $\longrightarrow$ 2,8,5,7-$C_{10}H_6Me(NO_2)CH(CO_2Et)_2$ (VIII) $\longrightarrow$ 2,8,5,7-$C_{10}H_6Me(NO_2)CH_2CO_2H$ (IX) $\longrightarrow$ I. Nine g. of III (prepd. from II, *C. A.* 24, 5296) is dissolved in concd. H_2SO_4, and the soln. cooled. $NaNO_2$ (9.2 g.) in 55 cc. H_2O is added drop by drop with stirring, followed by 48 g. HNO_3 (40° Bé). IV, crystd. from glacial AcOH, m. 101–0.5°, yield, 8.3 g. Four g. *p*-$MeC_6H_4SO_2Cl$ is added to a mixt. of 5 g. of IV and 0.5 g. PhNMe$_2$ to give V which, prptd. from dil. HCl (1:5) with dil. NH_4OH (1:5) and crystd. from glacial AcOH, m. 166.5–56°, yield 3.4 g. Six g. V, treated with 5.1 g. $CH_2(CO_2H)_2$ and 0.66 g. Na, gives 4.4 g. VI. Crystd. from glacial AcOH, it m. 203.0°. Heating 3 g. VI with glacial AcOH and H_2SO_4 gives 2.2 g. VII, m. (decompn.) 160–76°. VII heated in pyridine gives a quant. yield of VIII, which, crystd. from EtOH, m. 163–5.5°. Ten g. VIII is reduced with $SnCl_2$ to give 2 g. of IX, which, crystd. from ligroin, m. 114–6°. I is obtained from IX by diazotizing and heating. I, recovered by steam distn. and crystd. from ligroin, m. 84–5°. The partial reduction of VIII gave a mixt. of products. The structure of one of these, *2,8-dimethyl-5-amino-7-nitronaphthalene* (X), was detd. by the following reactions: X $\longrightarrow$ 2,8,7-$C_{10}H_5Me_2NO_3$ (XI) $\longrightarrow$ 2,8,7-$C_{10}H_5Me_2NH_2$ (XII) $\longrightarrow$ 2,8,7-$C_{10}H_5Me_2OH$ (XIII). X, purified as the *perchlorate* and obtained as the free base by treatment with NH_4OH, m. 151–3°. The *Ac deriv.*, crystd. from EtOH, m. 56.5–58. 220–2°. XI, obtained from X by diazotization and crystd. from EtOH, m. 207–8°. Diazotization of XII and removal Reduction of XI with Fe filings and AcOH gives XII as an oil which would not solidify. The *Ac deriv.* of XII, crystd. from EtOH, m. 207–8°. Diazotization of XII and removal of the diazo group does not give I but another *dimethylnaphthalene*, m. 42–3°, of undetd. constitution. XIII, obtained by diazotization of XII followed by decompn. with dil.



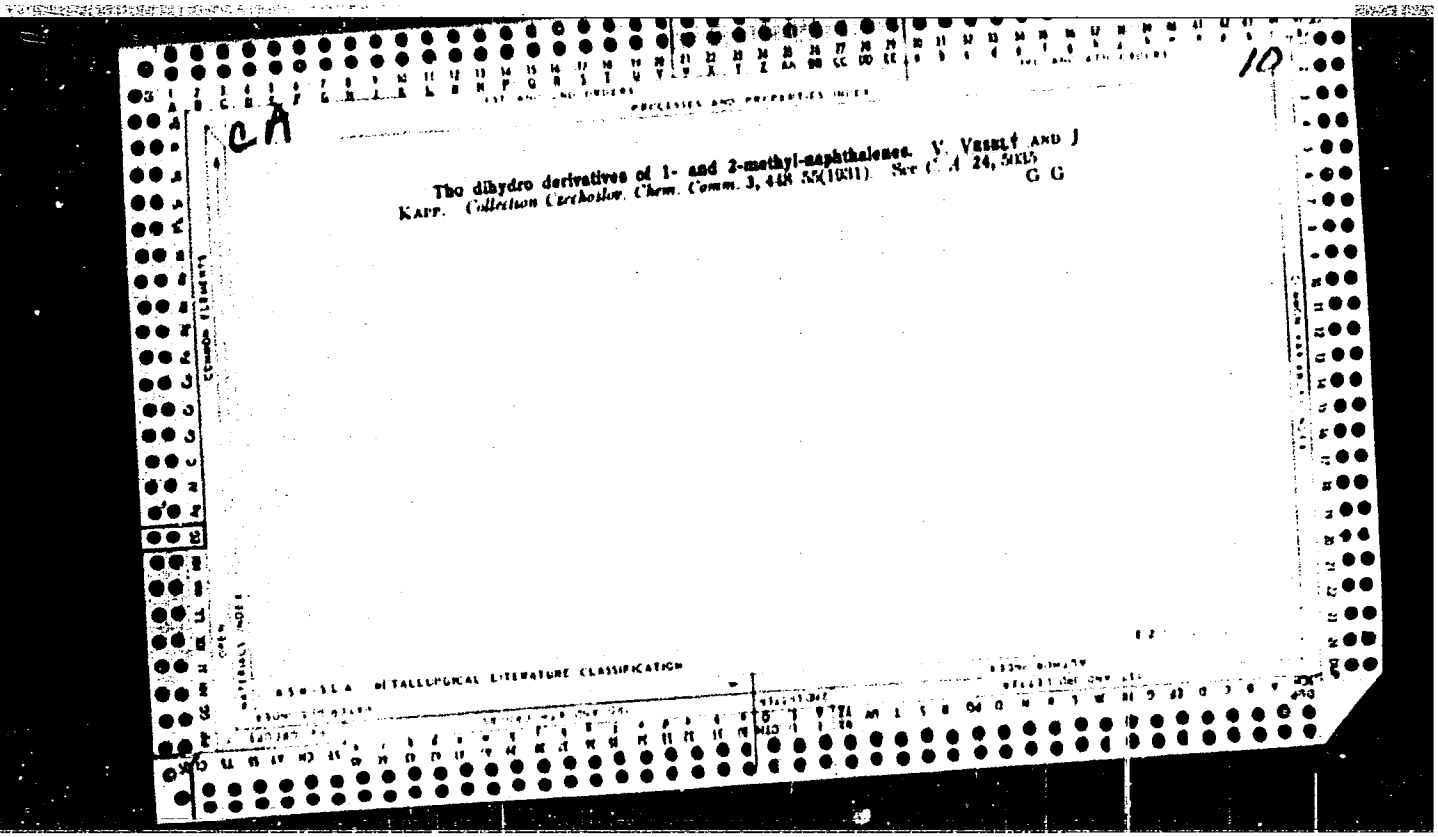
H_2SO_4, m. 138–40°. XIII coupled with diazotized *p*-nitroaniline gives a *colorless compd.* This failure to form a colored compd. is considered conclusive proof that XIII and not 2,8,5-$C_{14}H_{16}N_2O$H is the correct structure of the 2,8-dimethylnaphthol (*C. A.* 8, 661). A new *method* is given for prepg. *2-methyl-8-aminonaphthalene* from III. The *picrate* of I, prepd. in EtOH, m. 114–7°.

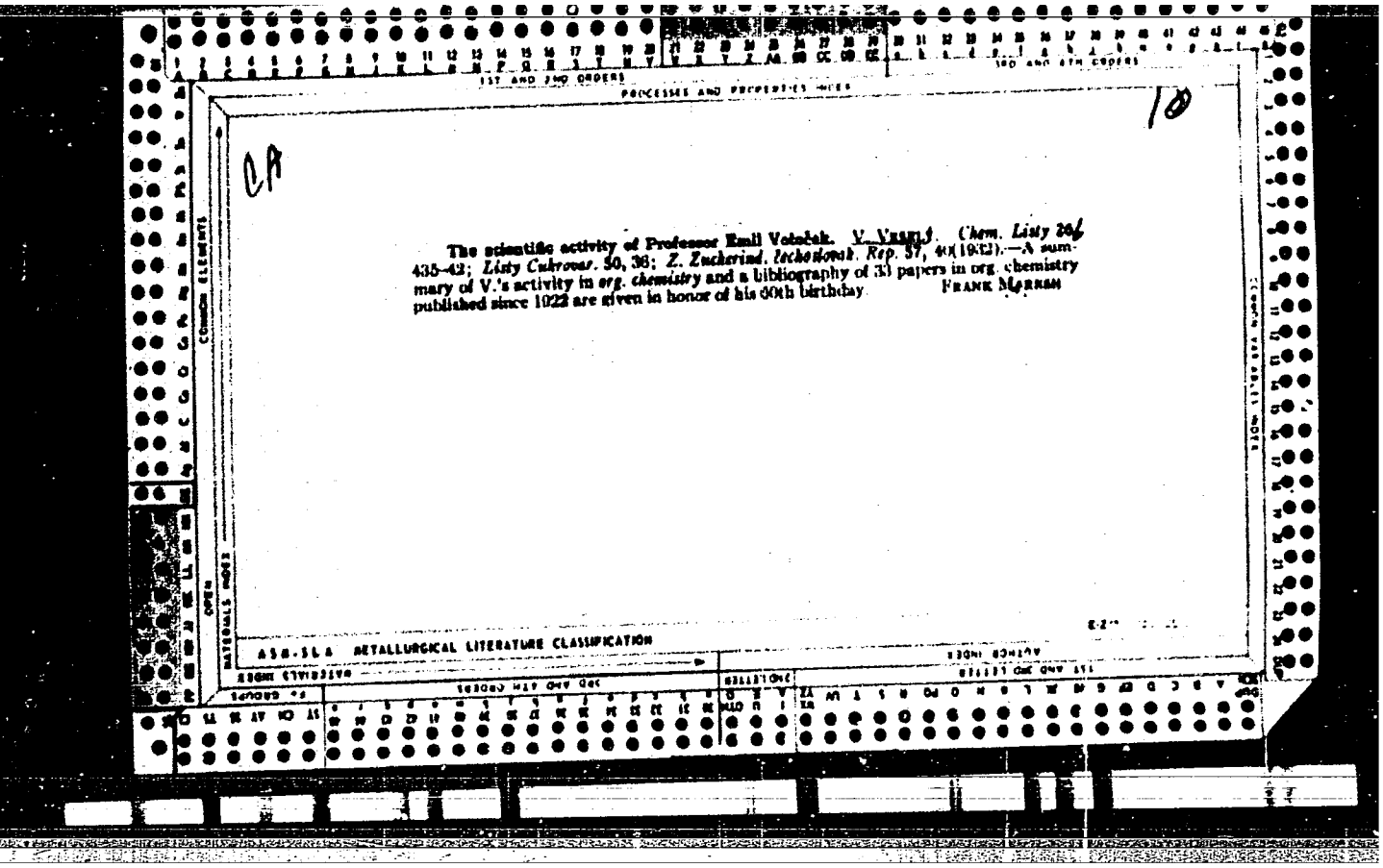
FELIX SAUNDERS



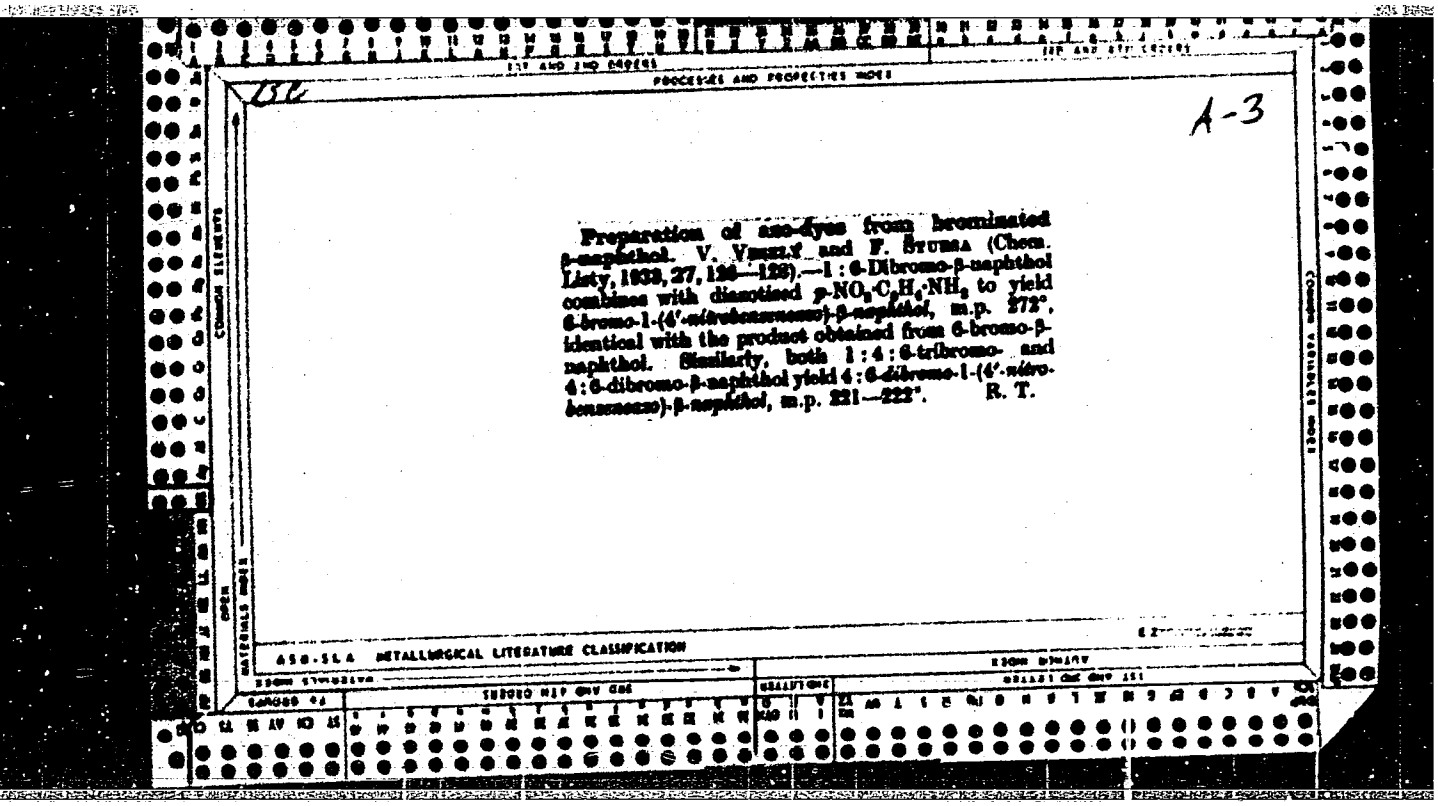
The preparation of 1,5- and 1,8-dimethylnaphthalene. V. Vesely and F. Sturza. *Collection Czechoslov. Chem. Comm.* 3, 430–1(1931).—*1,5-Dimethylnaphthalene* (I) is obtained as follows: 17 g. 1,5-$C_{10}H_6MeBr$ (*C. A.* 24, 3008) is added to the Grignard reagent prepd. by treating 1.8 g. Mg turnings in dry Et_2O with MeI (N atm.). After the reaction has stopped 12 g. Me_2SO_4 in Et_2O is added. The mixt. heats spontaneously and then sets to a thick mass. It is heated on the water bath 2 hrs. and then decomposed with dil. H_2SO_4 (1:5). The Et_2O solu. is sepd. and dried with Na_2SO_4. After evapn. of the Et_2O, I is obtained in 3.8 g. yield by steam distn. and, when crystd. from MeOH, m. 77–8°. The *picrate* of I, prepd. by the addn. of the calcd. amt. of picric acid to I in EtOH, m. 137–8°. *1,8-Dimethylnaphthalene* (II), prepd. from 1.7 g. 1,8-$C_{10}H_6MeBr$ by the same procedure (yield 0.4 g.), is an oil which does not solidify at −20°. The *picrate* (III) of II m. 143–4°. A mixt. of III and the picrate of 1-$C_{10}H_7Me$ (m. 141–2°) showed considerable depression.

Felix Saunders





The scientific activity of Professor Emil Votoček. V. Vesely. *Chem. Listy* 36, 435–42; *Listy Cukrovar.* 50, 38; *Z. Zucherind. Tschechoslovak. Rep.* 57, 40(1932).—A summary of V.'s activity in *org. chemistry* and a bibliography of 31 papers in org. chemistry published since 1922 are given in honor of his 60th birthday. FRANK MARRAM



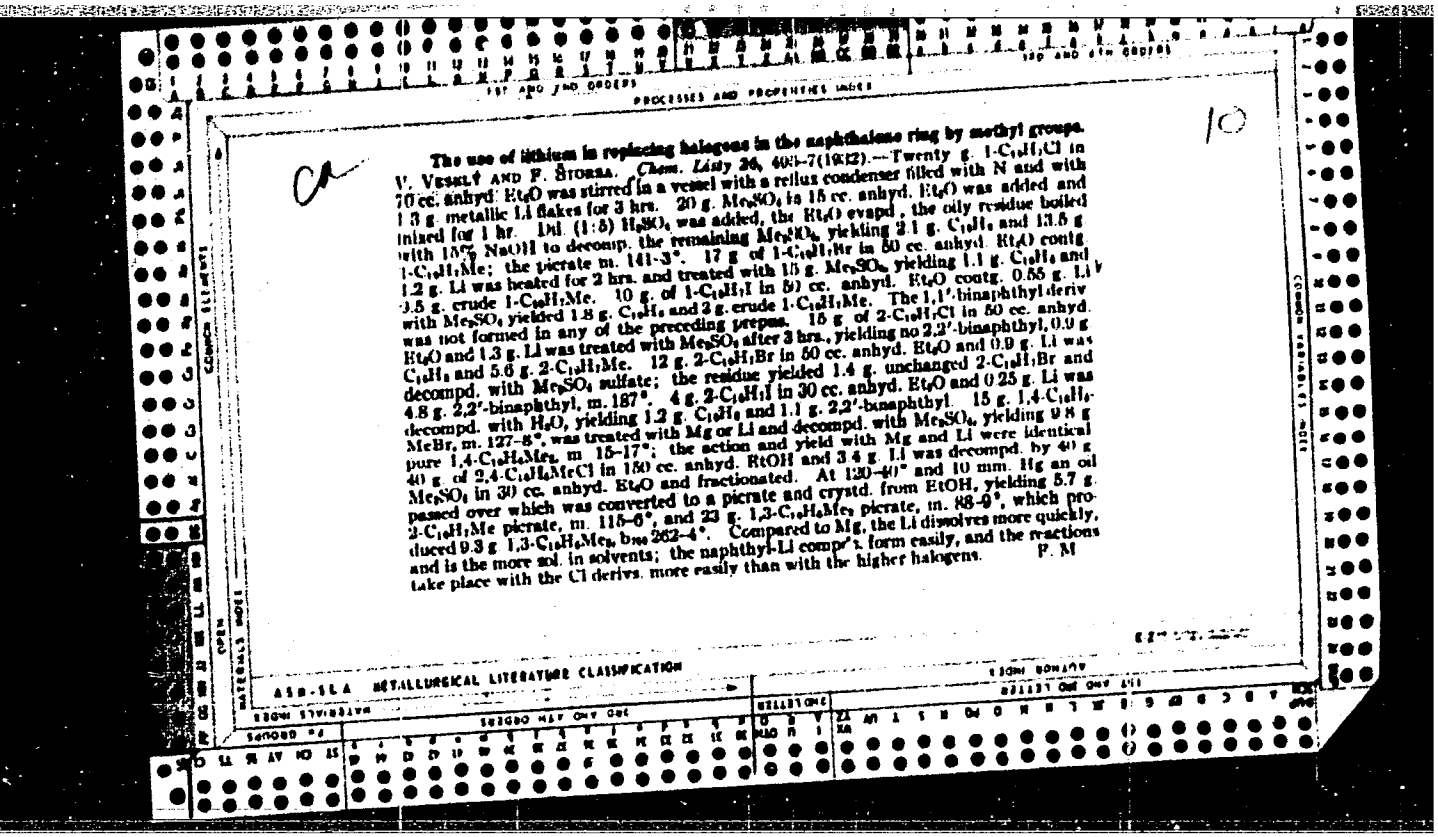
A-3

Preparation of azo-dyes from brominated β-naphthol. V. Vesely and F. Strumza (Chem. Listy, 1933, 27, 128—129).—1 : 6-Dibromo-β-naphthol combines with diazotised p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ to yield 6-bromo-1-(4'-*nitrobenzeneazo*)-β-*naphthol*, m.p. 272°, identical with the product obtained from 6-bromo-β-naphthol. Similarly, both 1 : 4 : 6-tribromo- and 4 : 6-dibromo-β-naphthol yield 4 : 6-*dibromo*-1-(4'-*nitrobenzeneazo*)-β-*naphthol*, m.p. 221—222°. R. T.

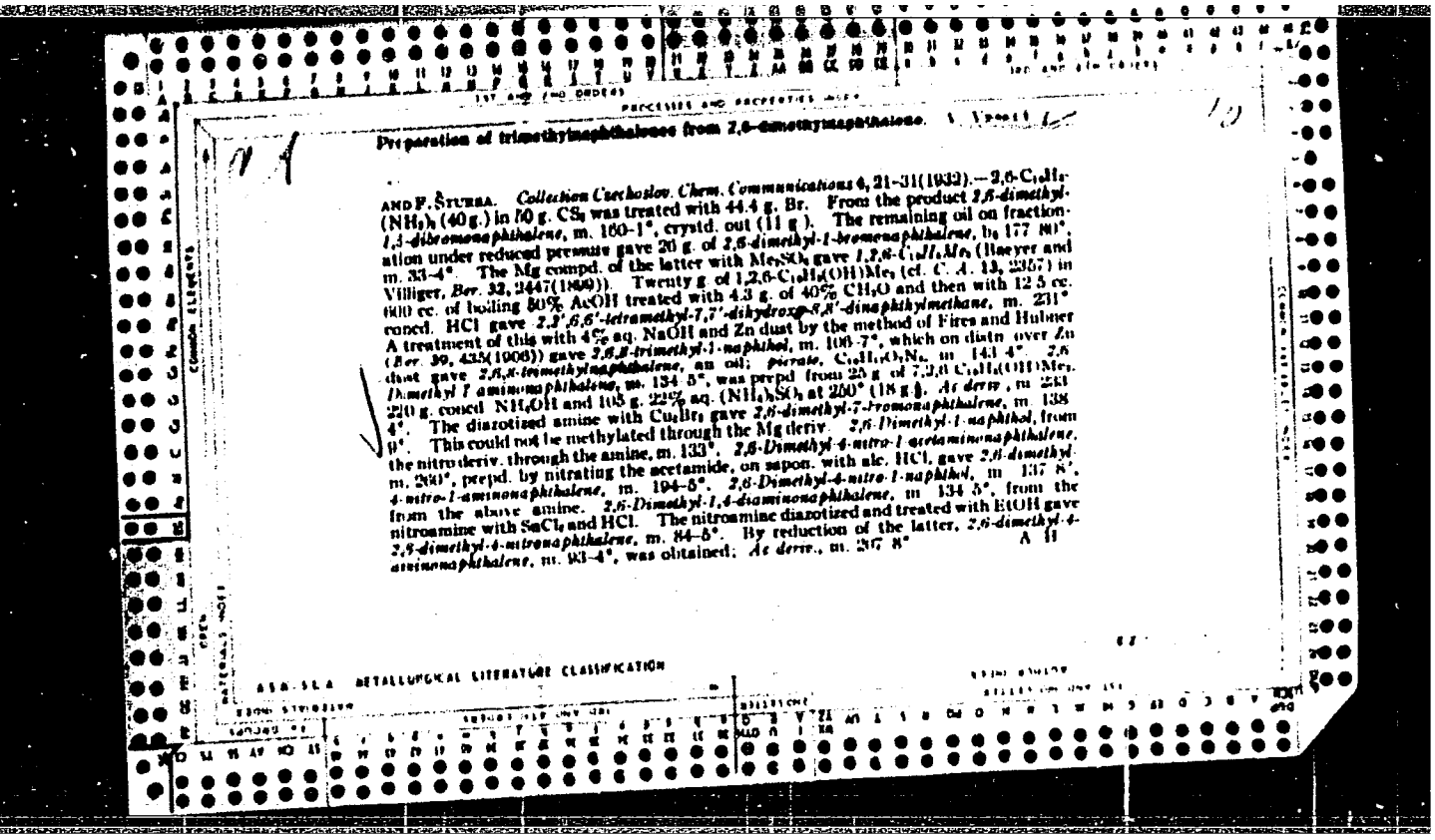
A-3

Derivatives of 1-phenylnaphthalene. V. VESELÝ and F. ŠTURSA (Coll. Czech. Chem. Comm., 1933, 5, 343—347).—Contrary to the orientation assigned by Weiss and Woidich (A., 1926, 809) $1\text{-}C_{10}H_7Ph$ with $Ac_2O\text{-}HNO_3$ (*d* 1·51) gives its 4-NO_2-*derivative*, m.p. 133°, reduced by Fe-AcOH to the 4-NH_2-*compound* (I), m.p. 73—74° (*Ac* derivative, m.p. 167—168°), which with $Ac_2O\text{-}HNO_3$ $\leq 30°$ affords the *Ac derivative*, m.p. 207—208°, of 3-*nitro-4-amino-1-phenylnaphthalene* (II), m.p. 151—153°, obtained by hydrolysis with conc. HCl. Reduction of (II) with $SnCl_2$-HCl gives the 3 : 4-*diamine*, m.p. 100—101°, the orientation of which is proved by the formation of the 3 : 4-*phenanthrazine*, m.p. 277—228°(?), by condensation with phenanthraquinone in AcOH. By the Sandmeyer reaction (I) gives 4-*bromo-1-phenylnaphthalene*, m.p. 76—77°. J. W. B.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



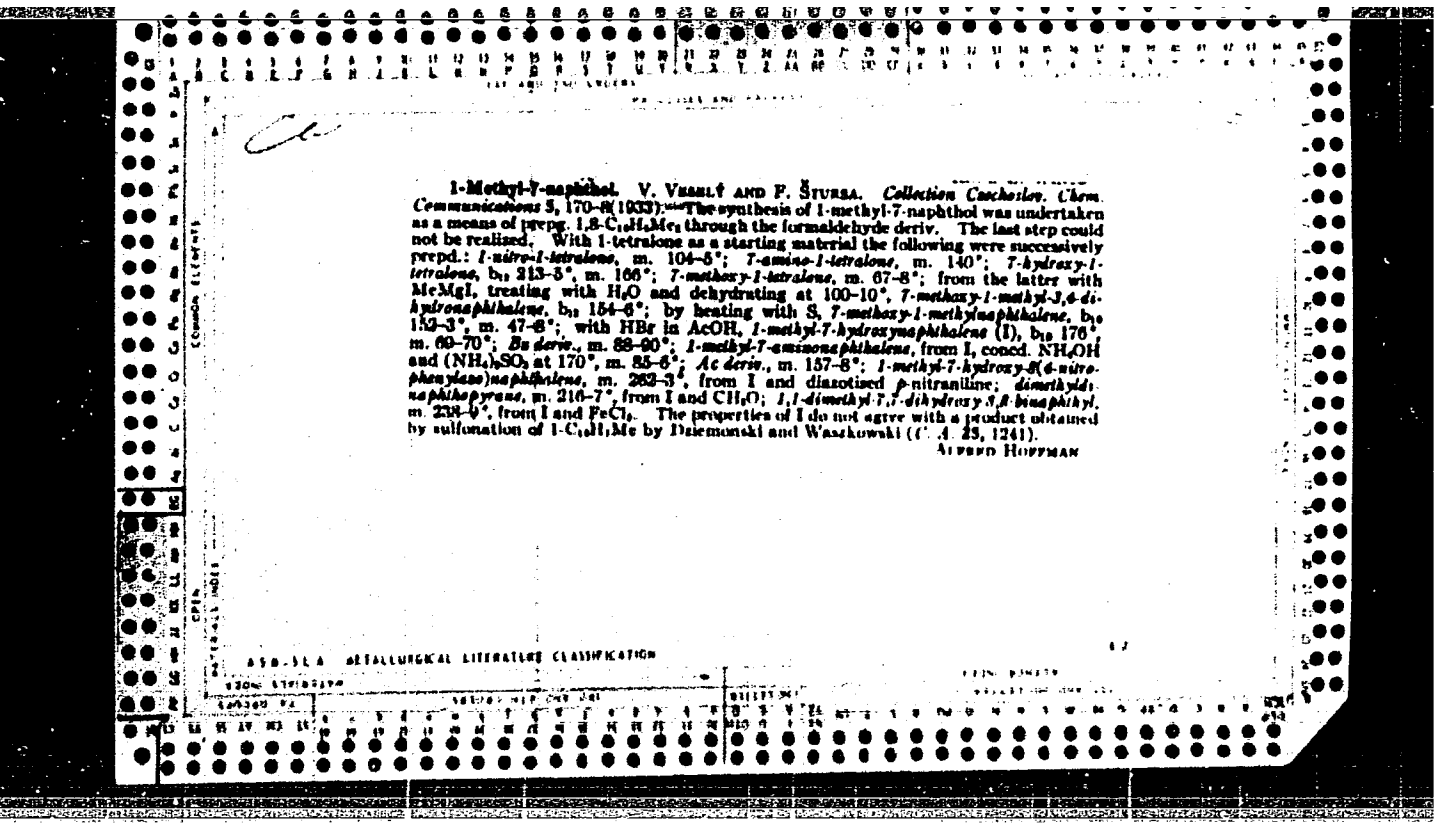
The use of lithium in replacing halogens in the naphthalene ring by methyl groups.
V. Veselý and F. Stozsa. *Chem. Listy* 26, 405-7(1932).—Twenty g. 1-$C_{10}H_7Cl$ in 70 cc. anhyd. Et_2O was stirred in a vessel with a reflux condenser filled with N and with 1.3 g. metallic Li flakes for 3 hrs. 20 g. Me_2SO_4 in 15 cc. anhyd. Et_2O was added and stirred for 1 hr. Dil. (1:5) H_2SO_4 was added, the Et_2O evapd., the oily residue boiled with 15% NaOH to decomp. the remaining Me_2SO_4, yielding 2.1 g. $C_{10}H_8$ and 13.5 g. 1-$C_{10}H_7Me$; the picrate m. 141-3°. 17 g. of 1-$C_{10}H_7Br$ in 50 cc. anhyd. Et_2O contg. 1.2 g. Li was heated for 2 hrs. and treated with 15 g. Me_2SO_4, yielding 1.1 g. $C_{10}H_8$ and 9.5 g. crude 1-$C_{10}H_7Me$. 10 g. of 1-$C_{10}H_7I$ in 50 cc. anhyd. Et_2O contg. 0.55 g. Li was treated with Me_2SO_4, yielded 1.8 g. $C_{10}H_8$ and 3 g. crude 1-$C_{10}H_7Me$. The 1,1'-binaphthyl deriv. was not formed in any of the preceding preps. 15 g. of 2-$C_{10}H_7Cl$ in 50 cc. anhyd. Et_2O and 1.3 g. Li was treated with Me_2SO_4 after 3 hrs., yielding no 2,2'-binaphthyl, 0.9 g. $C_{10}H_8$ and 5.6 g. 2-$C_{10}H_7Me$. 12 g. 2-$C_{10}H_7Br$ in 50 cc. anhyd. Et_2O and 0.9 g. Li was decompd. with Me_2SO_4 sulfate; the residue yielded 1.4 g. unchanged 2-$C_{10}H_7Br$ and 4.8 g. 2,2'-binaphthyl, m. 187°. 4 g. 2-$C_{10}H_7I$ in 30 cc. anhyd. Et_2O and 0.25 g. Li was decompd. with H_2O, yielding 1.2 g. $C_{10}H_8$ and 1.1 g. 2,2'-binaphthyl. 15 g. 1,4-$C_{10}H_6$-MeBr, m. 127-8°, was treated with Mg or Li and decompd. with Me_2SO_4, yielding 9.8 g. pure 1,4-$C_{10}H_6Me_2$, m. 15-17°; the action and yield with Mg and Li were identical. 40 g. of 2,4-$C_{10}H_6MeCl$ in 150 cc. anhyd. EtOH and 3.4 g. Li was decompd. by 40 g. Me_2SO_4 in 30 cc. anhyd. Et_2O and fractionated. At 130-40° and 10 mm. Hg an oil passed over which was converted to a picrate and crystd. from EtOH, yielding 5.7 g. 2-$C_{10}H_7Me$ picrate, m. 115-6°, and 23 g. 1,3-$C_{10}H_6Me_2$ picrate, m. 88-9°, which produced 9.3 g. 1,3-$C_{10}H_6Me_2$, b$_{760}$ 262-4°. Compared to Mg, the Li dissolves more quickly, and is the more sol. in solvents; the naphthyl-Li compds. form easily, and the reactions take place with the Cl derivs. more easily than with the higher halogens. P. M



Preparation of trimethylnaphthalenes from 2,6-dimethylnaphthalene.

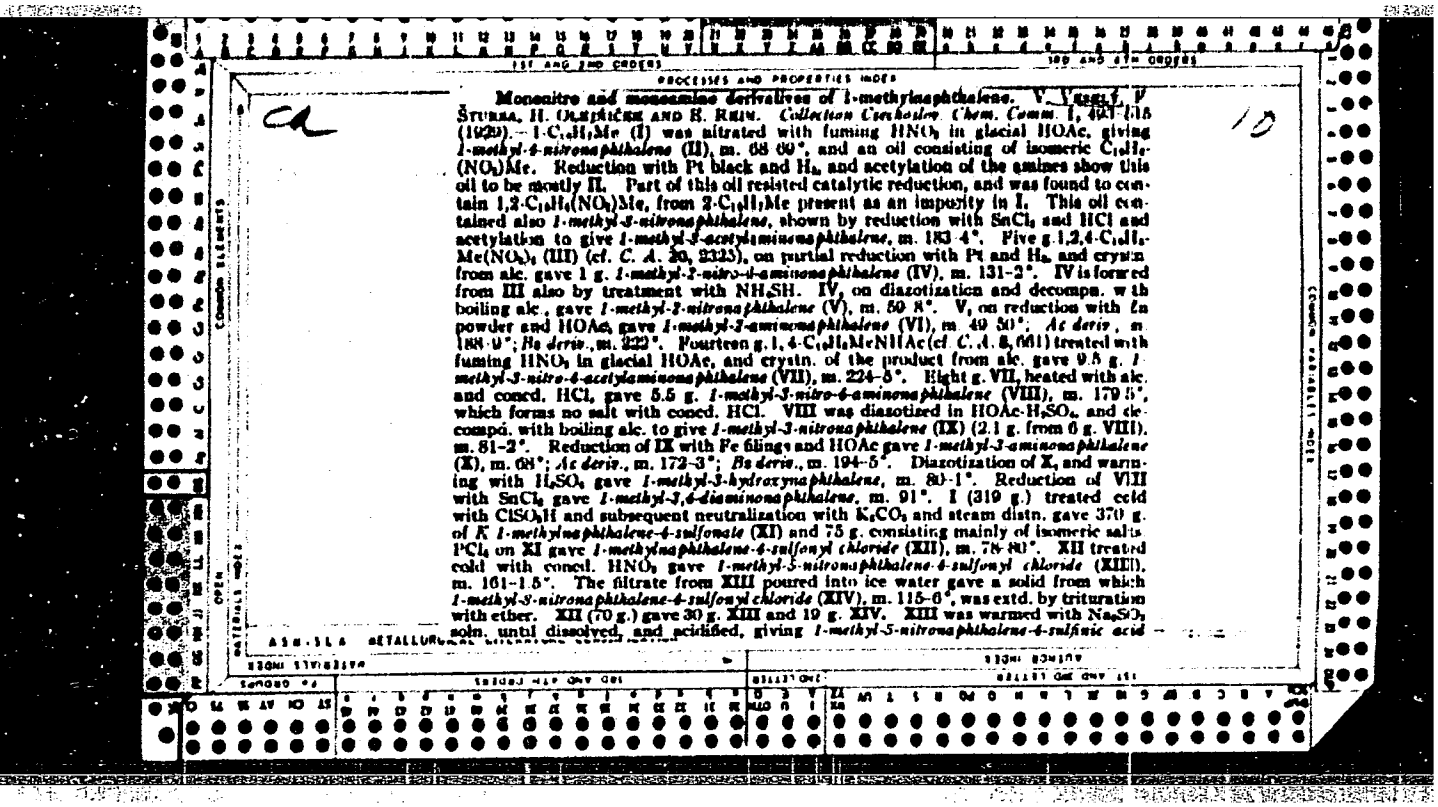
AND F. ŠTURBA. *Collection Czechoslov. Chem. Communications* 4, 21-31(1932).—2,6-$C_{10}H_6$-(NH_2)$_2$ (40 g.) in 80 g. CS_2 was treated with 44.4 g. Br. From the product *2,6-dimethyl-1,3-dibromonaphthalene*, m. 160-1°, crystd. out (11 g.). The remaining oil on fractionation under reduced pressure gave 20 g. of *2,6-dimethyl-1-bromonaphthalene*, b$_{15}$ 177-80°, m. 33-4°. The Mg compd. of the latter with Me_2SO_4 gave *1,2,6-*$C_{10}H_5Me_3$ (Baeyer and Villiger, *Ber.* 32, 3447(1899)). Twenty g. of 1,2,6-$C_{10}H_5(OH)Me_2$ (cf. *C. A.* 13, 2357) in 600 cc. of boiling 80% AcOH treated with 4.3 g. of 40% CH_2O and then with 12.5 cc. concd. HCl gave *2,3',6,6'-tetramethyl-7,7'-dihydroxy-8,8'-dinaphthylmethane*, m. 231°. A treatment of this with 4% aq. NaOH and Zn dust by the method of Fires and Hubner (*Ber.* 39, 435(1906)) gave *2,6,8-trimethyl-1-naphthol*, m. 106-7°, which on distn. over Zn dust gave *2,6,8-trimethylnaphthalene*, an oil; *picrate*, $C_{19}H_{19}O_7N_3$, m. 143-4°. *2,6-Dimethyl-1-aminonaphthalene*, m. 134-5°, was prepd. from 25 g. of 7,3,0 $C_{10}H_5(OH)Me_2$, 250 g. concd. NH_4OH and 105 g. 22% aq. $(NH_4)_2SO_3$ at 200° (18 g.). *Ac deriv.*, m. 233-4°. The diazotized amine with $CuBr_2$ gave *2,6-dimethyl-1-bromonaphthalene*, m. 138-9°. This could not be methylated through the Mg deriv. *2,6-Dimethyl-1-naphthol*, from the nitro deriv. through the amine, m. 133°. *2,6-Dimethyl-4-nitro-1-acetaminonaphthalene*, m. 280°, prepd. by nitrating the acetamide, on sapon. with alc. HCl, gave *2,6-dimethyl-4-nitro-1-aminonaphthalene*, m. 194-5°. *2,6-Dimethyl-4-nitro-1-naphthol*, m. 137-8°, from the above amine. *2,6-Dimethyl-1,4-diaminonaphthalene*, m. 134-5°, from the nitrosamine with $SnCl_2$ and HCl. The nitrosamine diazotized and treated with EtOH gave *2,6-dimethyl-4-nitronaphthalene*, m. 84-5°. By reduction of the latter, *2,6-dimethyl-4-aminonaphthalene*, m. 93-4°, was obtained; *Ac deriv.*, m. 207-8°

A II



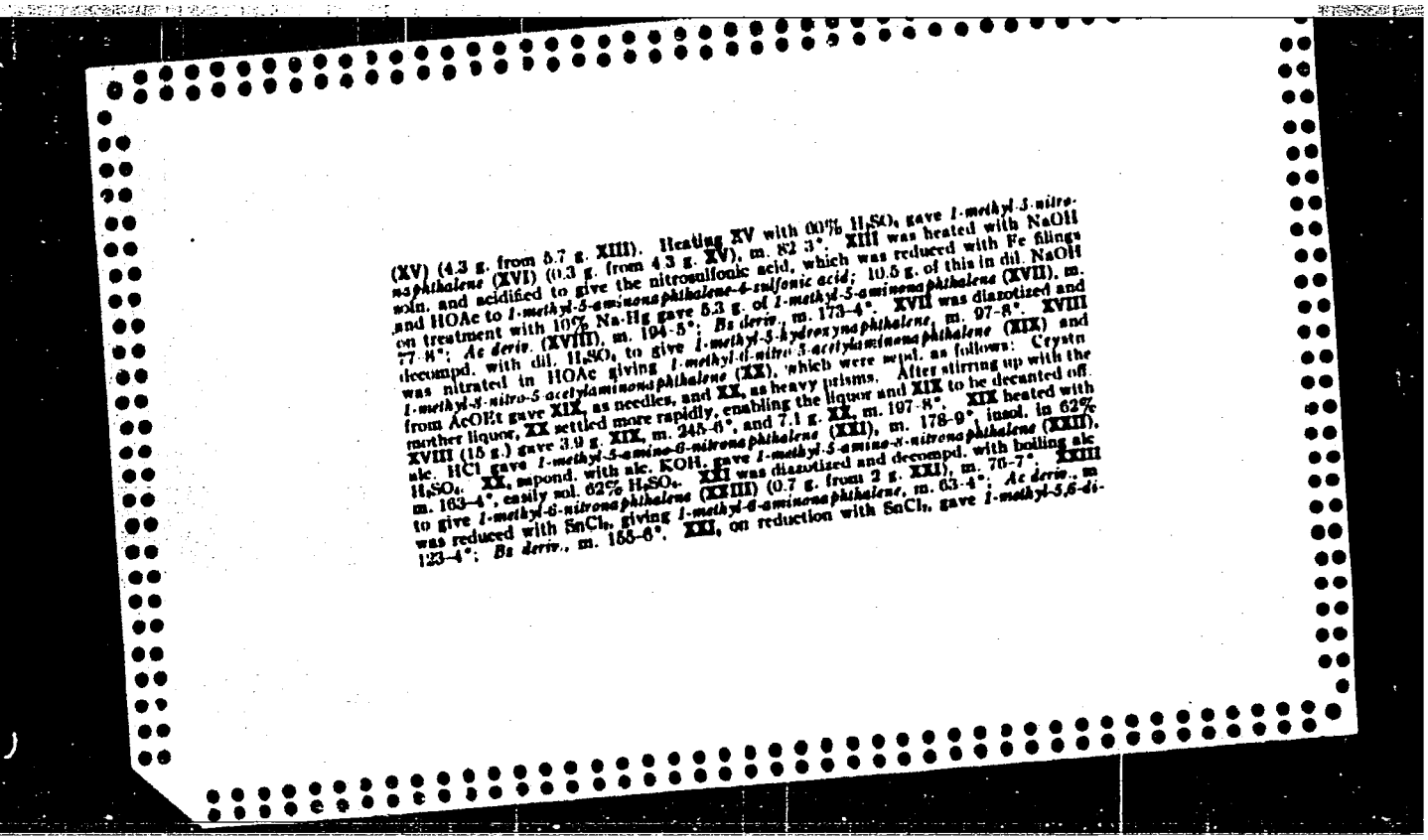
1-Methyl-7-naphthol. V. Vesely and F. Stursa. *Collection Czechoslov. Chem. Communications* 5, 170–8(1933).—The synthesis of 1-methyl-7-naphthol was undertaken as a means of prepg. 1,8-$C_{10}H_5Me_2$ through the formaldehyde deriv. The last step could not be realized. With 1-tetralone as a starting material the following were successively prepd.: *1-nitro-1-tetralone*, m. 104–5°; *7-amino-1-tetralone*, m. 140°; *7-hydroxy-1-tetralone*, b_{12} 213–5°, m. 166°; *7-methoxy-1-tetralone*, m. 67–8°; from the latter with MeMgI, treating with H_2O and dehydrating at 100–10°, *7-methoxy-1-methyl-3,4-dihydronaphthalene*, b_{12} 154–6°; by heating with S, *7-methoxy-1-methylnaphthalene*, b_{12} 152–3°, m. 47–8°; with HBr in AcOH, *1-methyl-7-hydroxynaphthalene* (I), b_{12} 176°, m. 69–70°; *Bz deriv.*, m. 88–90°; *1-methyl-7-aminonaphthalene*, from I, concd. NH_4OH and $(NH_4)_2SO_3$ at 170°, m. 85–6°; *Ac deriv.*, m. 157–8°; *1-methyl-7-hydroxy-8(6-nitrophenylazo)naphthalene*, m. 262–3°, from I and diazotized *p*-nitraniline; *dimethyldinaphthopyrane*, m. 216–7°, from I and CH_2O; *1,1-dimethyl-7,7-dihydroxy-8,8-binaphthyl*, m. 238–9°, from I and $FeCl_3$. The properties of I do not agree with a product obtained by sulfonation of 1-$C_{10}H_7Me$ by Dziewonski and Waszkowski (*C. A.* 25, 1241).

Alfred Hoffman

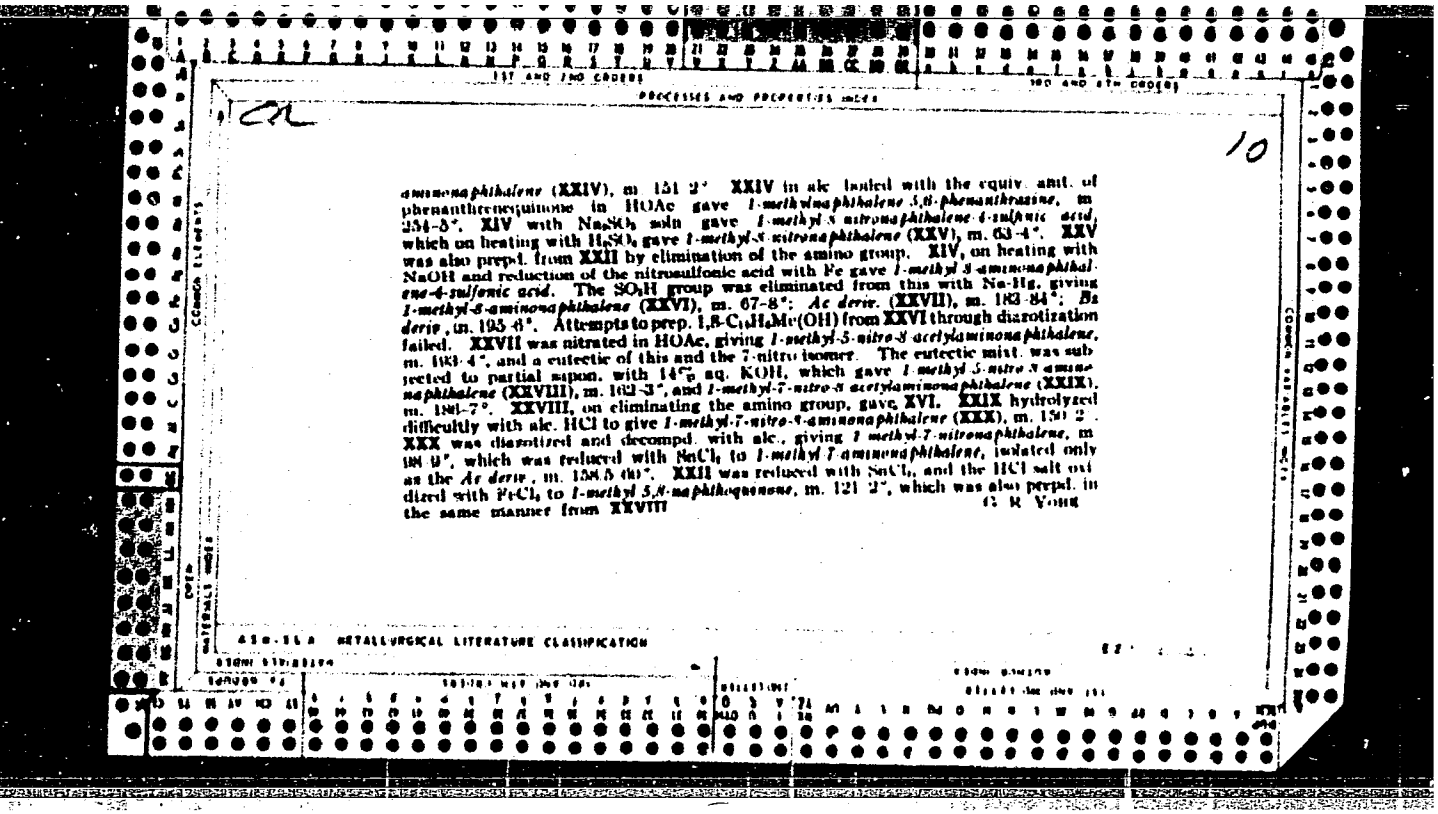


PROCESSES AND PROPERTIES INDEX

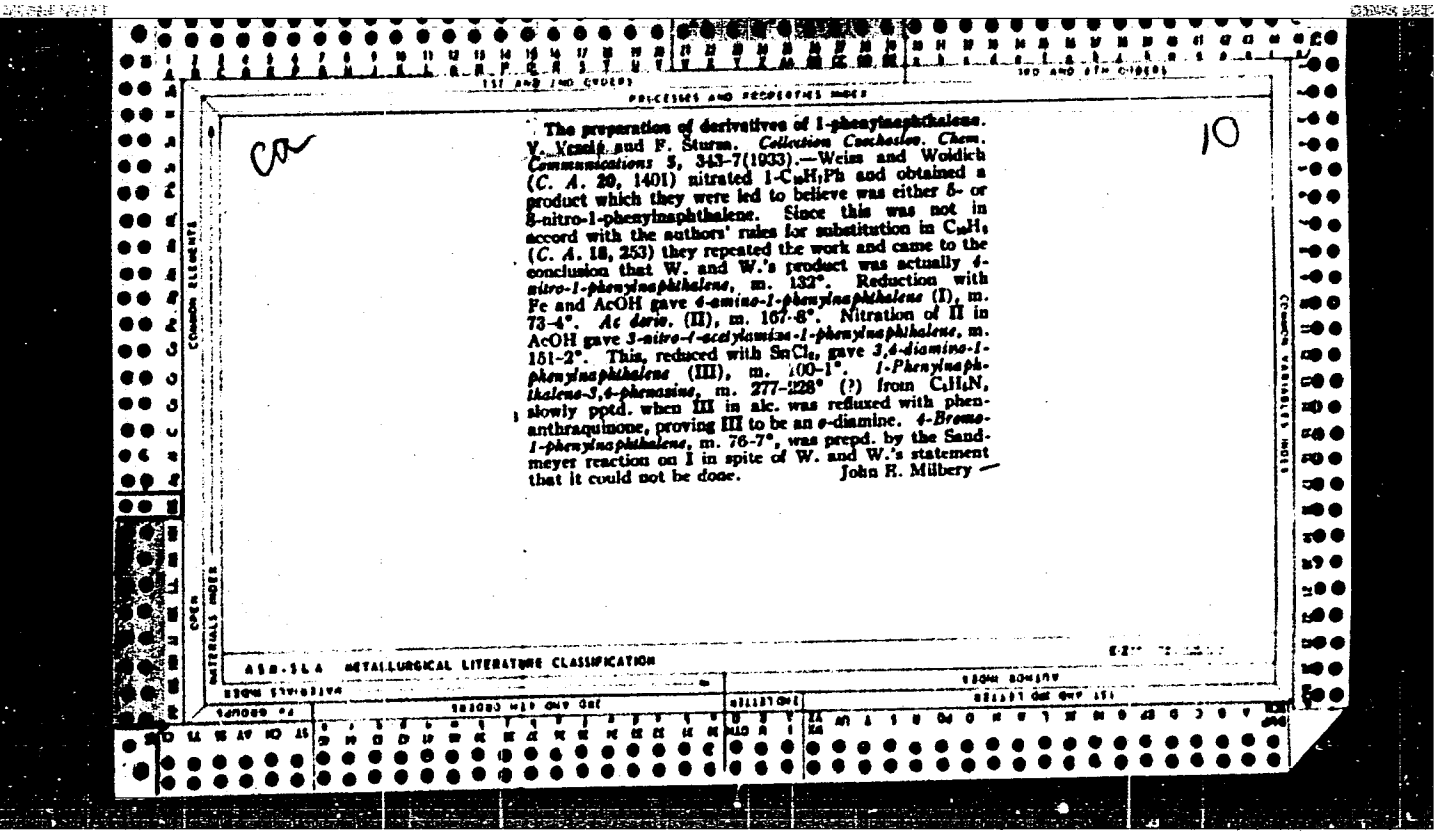
Mononitro and monoamino derivatives of 1-methylnaphthalene. V. Vesely, V. Štursa, H. Olejníček and R. Rein. *Collection Czechoslov. Chem. Comm.* 1, 401–16 (1929).—1-$C_{10}H_7Me$ (I) was nitrated with fuming HNO_3 in glacial HOAc, giving *1-methyl-4-nitronaphthalene* (II), m. 68–69°, and an oil consisting of isomeric $C_{10}H_6(NO_2)Me$. Reduction with Pt black and H_2, and acetylation of the amines show this oil to be mostly II. Part of this oil resisted catalytic reduction, and was found to contain 1,2-$C_{10}H_6(NO_2)Me$, from 2-$C_{10}H_7Me$ present as an impurity in I. This oil contained also *1-methyl-3-nitronaphthalene*, shown by reduction with $SnCl_2$ and HCl and acetylation to give *1-methyl-3-acetylaminonaphthalene*, m. 183–4°. Five g. 1,2,4-$C_{10}H_5Me(NO_2)_2$ (III) (*cf. C. A.* 20, 2325), on partial reduction with Pt and H_2, and crystn. from alc. gave 1 g. *1-methyl-2-nitro-4-aminonaphthalene* (IV), m. 131–2°. IV is formed from III also by treatment with NH_4SH. IV, on diazotization and decompn. with boiling alc., gave *1-methyl-2-nitronaphthalene* (V), m. 59–8°. V, on reduction with Zn powder and HOAc, gave *1-methyl-2-aminonaphthalene* (VI), m. 49–50°. *Ac deriv.*, m. 188–9°; *Bz deriv.*, m. 222°. Fourteen g. 1,4-$C_{10}H_6MeNHAc$ (*cf. C. A.* 8, 661) treated with fuming HNO_3 in glacial HOAc, and crystn. of the product from alc. gave 9.5 g. *1-methyl-3-nitro-4-acetylaminonaphthalene* (VII), m. 224–5°. Eight g. VII, heated with alc. and concd. HCl, gave 5.5 g. *1-methyl-3-nitro-4-aminonaphthalene* (VIII), m. 179.5°, which forms no salt with concd. HCl. VIII was diazotized in HOAc-H_2SO_4, and decompd. with boiling alc. to give *1-methyl-3-nitronaphthalene* (IX) (2.1 g. from 6 g. VIII), m. 81–2°. Reduction of IX with Fe filings and HOAc gave *1-methyl-3-aminonaphthalene* (X), m. 68°; *Ac deriv.*, m. 172–3°; *Bz deriv.*, m. 194–5°. Diazotization of X, and warming with H_2SO_4, gave *1-methyl-3-hydroxynaphthalene*, m. 80–1°. Reduction of VIII with $SnCl_2$ gave *1-methyl-3,4-diaminonaphthalene*, m. 91°. I (319 g.) treated cold with $ClSO_3H$ and subsequent neutralization with K_2CO_3 and steam distn. gave 370 g. of *K 1-methylnaphthalene-4-sulfonate* (XI) and 75 g. consisting mainly of isomeric salts. PCl_5 on XI gave *1-methylnaphthalene-4-sulfonyl chloride* (XII), m. 78–80°. XII treated cold with concd. HNO_3 gave *1-methyl-3-nitronaphthalene-4-sulfonyl chloride* (XIII), m. 161–1.5°. The filtrate from XIII poured into ice water gave a solid from which *1-methyl-3-nitronaphthalene-4-sulfonyl chloride* (XIV), m. 115–6°, was extd. by trituration with ether. XII (70 g.) gave 30 g. XIII and 19 g. XIV. XIII was warmed with Na_2SO_3 soln. until dissolved, and acidified, giving *1-methyl-3-nitronaphthalene-4-sulfinic acid*



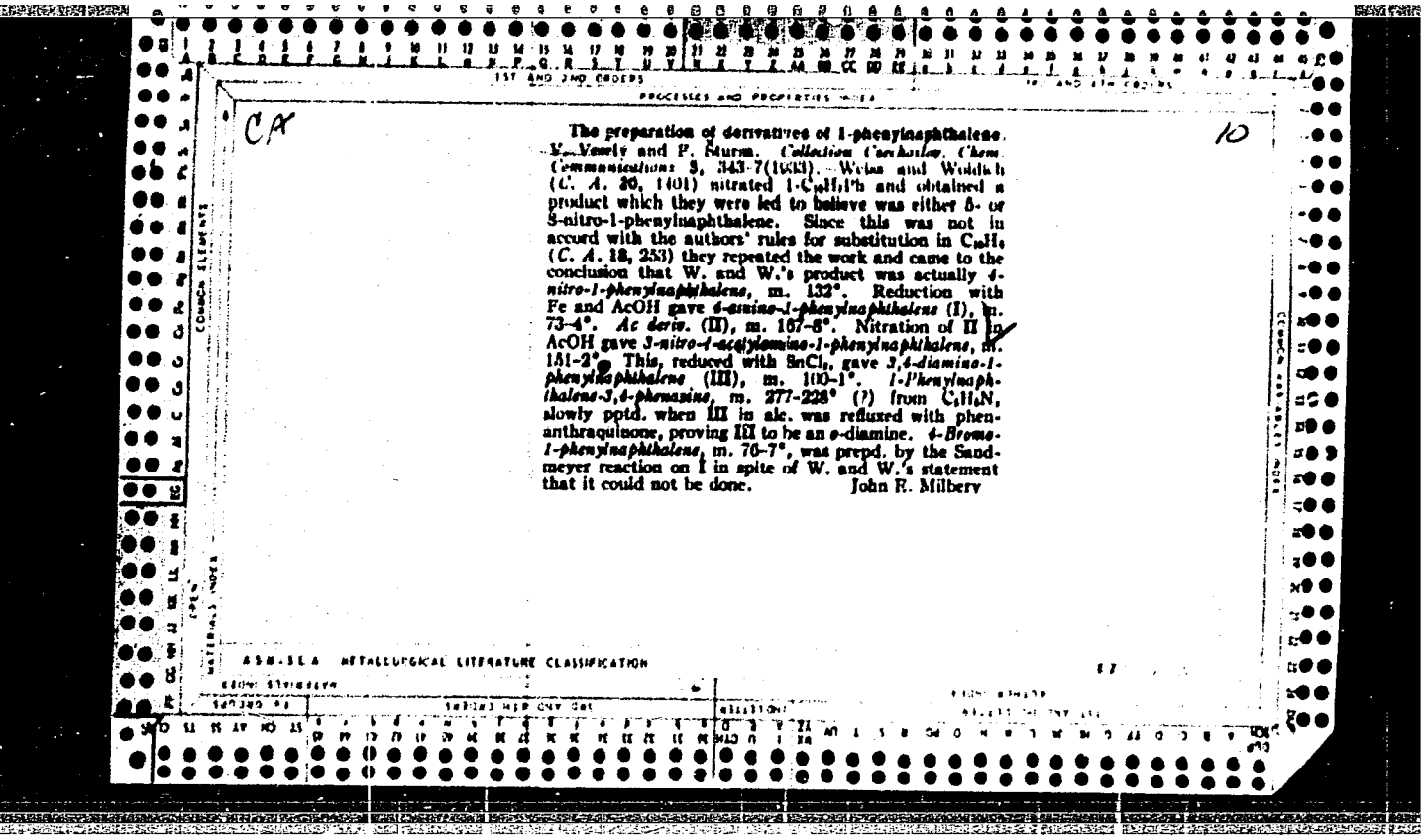
(XV) (4.3 g. from 5.7 g. XIII). Heating XV with 60% H_2SO_4 gave *1-methyl-5-nitro-*
naphthalene (XVI) (0.3 g. from 4.3 g. XV), m. 82.3°. XIII was heated with NaOH
soln. and acidified to give the nitrosulfonic acid, which was reduced with Fe filings
and HOAc to *1-methyl-5-aminonaphthalene-6-sulfonic acid*; 10.5 g. of this in dil. NaOH
on treatment with 10% Na-Hg gave 5.3 g. of *1-methyl-5-aminonaphthalene* (XVII), m.
77-8°; *Ac deriv.* (XVIII), m. 194-5°; *Bz deriv.*, m. 173-4°. XVII was diazotized and
decompd. with dil. H_2SO_4 to give *1-methyl-5-hydroxynaphthalene*, m. 97-8°. XVIII
was nitrated in HOAc giving *1-methyl-6-nitro-5-acetylaminonaphthalene* (XIX), which were sepd. as follows: Crystn
1-methyl-8-nitro-5-acetylaminonaphthalene (XX), as needles, and XX, as heavy prisms. After stirring up with the
from AcOEt gave XIX, as needles, and XX, as heavy prisms. After stirring up with the
mother liquor, XX settled more rapidly, enabling the liquor and XIX to be decanted off.
XVIII (15 g.) gave 3.9 g. XIX, m. 245-6°, and 7.1 g. XX, m. 197-8°. XIX heated with
alc. HCl gave *1-methyl-5-amino-6-nitronaphthalene* (XXI), m. 178-9°, insol. in 62%
H_2SO_4. XX, sapond. with alc. KOH, gave *1-methyl-5-amino-8-nitronaphthalene* (XXII),
m. 163-4°, easily sol. 62% H_2SO_4. XXI was diazotized and decompd. with boiling alc.
to give *1-methyl-6-nitronaphthalene* (XXIII) (0.7 g. from 2 g. XXI), m. 76-7°. XXIII
was reduced with $SnCl_2$, giving *1-methyl-6-aminonaphthalene*, m. 63-4°; *Ac deriv.*, m.
123-4°; *Bz deriv.*, m. 155-6°. XXI, on reduction with $SnCl_2$, gave *1-methyl-5,6-di-*



aminonaphthalene (XXIV), m. 151.2°. XXIV in alc. boiled with the equiv. amt. of phenanthrenequinone in HOAc gave *1-methylnaphthalene-5,6-phenanthrazine*, m. 254–5°. XIV with Na_2SO_3 soln. gave *1-methyl-8-nitronaphthalene-4-sulfonic acid*, which on heating with H_2SO_4 gave *1-methyl-8-nitronaphthalene* (XXV), m. 63–4°. XXV was also prepd. from XXII by elimination of the amino group. XIV, on heating with NaOH and reduction of the nitrosulfonic acid with Fe gave *1-methyl-8-aminonaphthalene-4-sulfonic acid*. The SO_3H group was eliminated from this with Na-Hg, giving *1-methyl-8-aminonaphthalene* (XXVI), m. 67–8°; *Ac deriv.* (XXVII), m. 183–84°; *Bz deriv.*, m. 195–6°. Attempts to prep. 1,8-$C_{11}H_9Me$(OH) from XXVI through diazotization failed. XXVII was nitrated in HOAc, giving *1-methyl-5-nitro-8-acetylaminonaphthalene*, m. 183–4°, and a eutectic of this and the 7-nitro isomer. The eutectic mixt. was subjected to partial sapon. with 14% aq. KOH, which gave *1-methyl-5-nitro-8-aminonaphthalene* (XXVIII), m. 182–3°, and *1-methyl-7-nitro-8-acetylaminonaphthalene* (XXIX), m. 186–7°. XXVIII, on eliminating the amino group, gave XVI. XXIX hydrolyzed difficultly with alc. HCl to give *1-methyl-7-nitro-8-aminonaphthalene* (XXX), m. 150.2°. XXX was diazotized and decomposed with alc., giving *1-methyl-7-nitronaphthalene*, m. 98.9°, which was reduced with $SnCl_2$ to *1-methyl-7-aminonaphthalene*, isolated only as the *Ac deriv.*, m. 158.5 (d)°. XXII was reduced with $SnCl_2$, and the HCl salt oxidized with $FeCl_3$ to *1-methyl-5,8-naphthaquinone*, m. 121.2°, which was also prepd. in the same manner from XXVIII. G. R. Yohe



The preparation of derivatives of 1-phenylnaphthalene. V. Vesely and F. Sturm. *Collection Czechoslov. Chem. Communications* 5, 343-7(1933).—Weiss and Woldrich (*C. A.* 20, 1401) nitrated 1-$C_{10}H_7Ph$ and obtained a product which they were led to believe was either 5- or 8-nitro-1-phenylnaphthalene. Since this was not in accord with the authors' rules for substitution in $C_{10}H_8$ (*C. A.* 18, 253) they repeated the work and came to the conclusion that W. and W.'s product was actually *4-nitro-1-phenylnaphthalene*, m. 132°. Reduction with Fe and AcOH gave *4-amino-1-phenylnaphthalene* (I), m. 73-4°. *Ac deriv.* (II), m. 167-8°. Nitration of II in AcOH gave *3-nitro-1-acetylamino-1-phenylnaphthalene*, m. 151-2°. This, reduced with $SnCl_2$, gave *3,4-diamino-1-phenylnaphthalene* (III), m. 100-1°. *1-Phenylnaphthalene-3,4-phenazine*, m. 277-228° (?) from $C_6H_6N_2$, slowly ppt'd. when III in alc. was refluxed with phenanthraquinone, proving III to be an *o*-diamine. *4-Bromo-1-phenylnaphthalene*, m. 76-7°, was prepd. by the Sandmeyer reaction on I in spite of W. and W.'s statement that it could not be done. John R. Millbery



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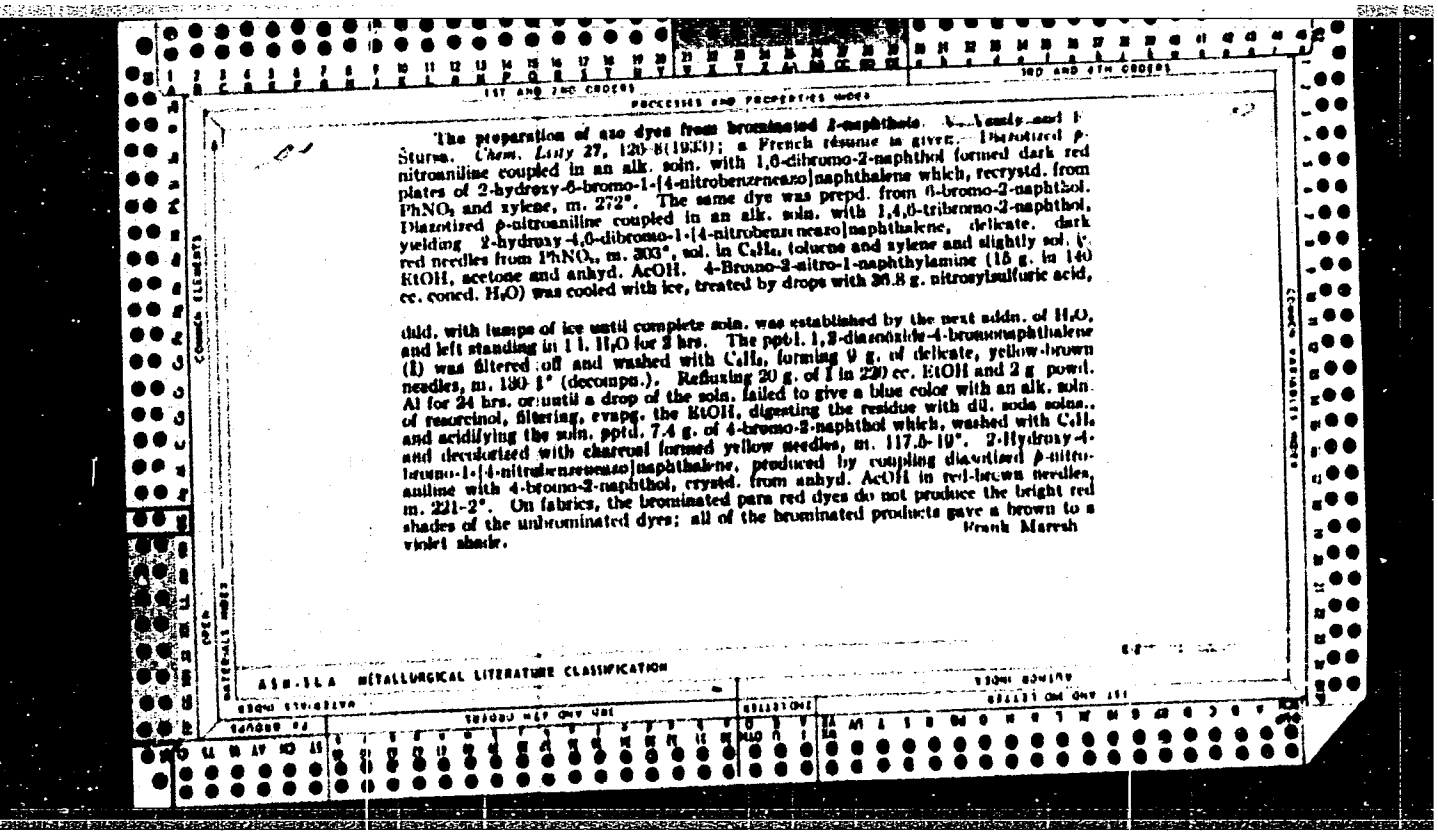
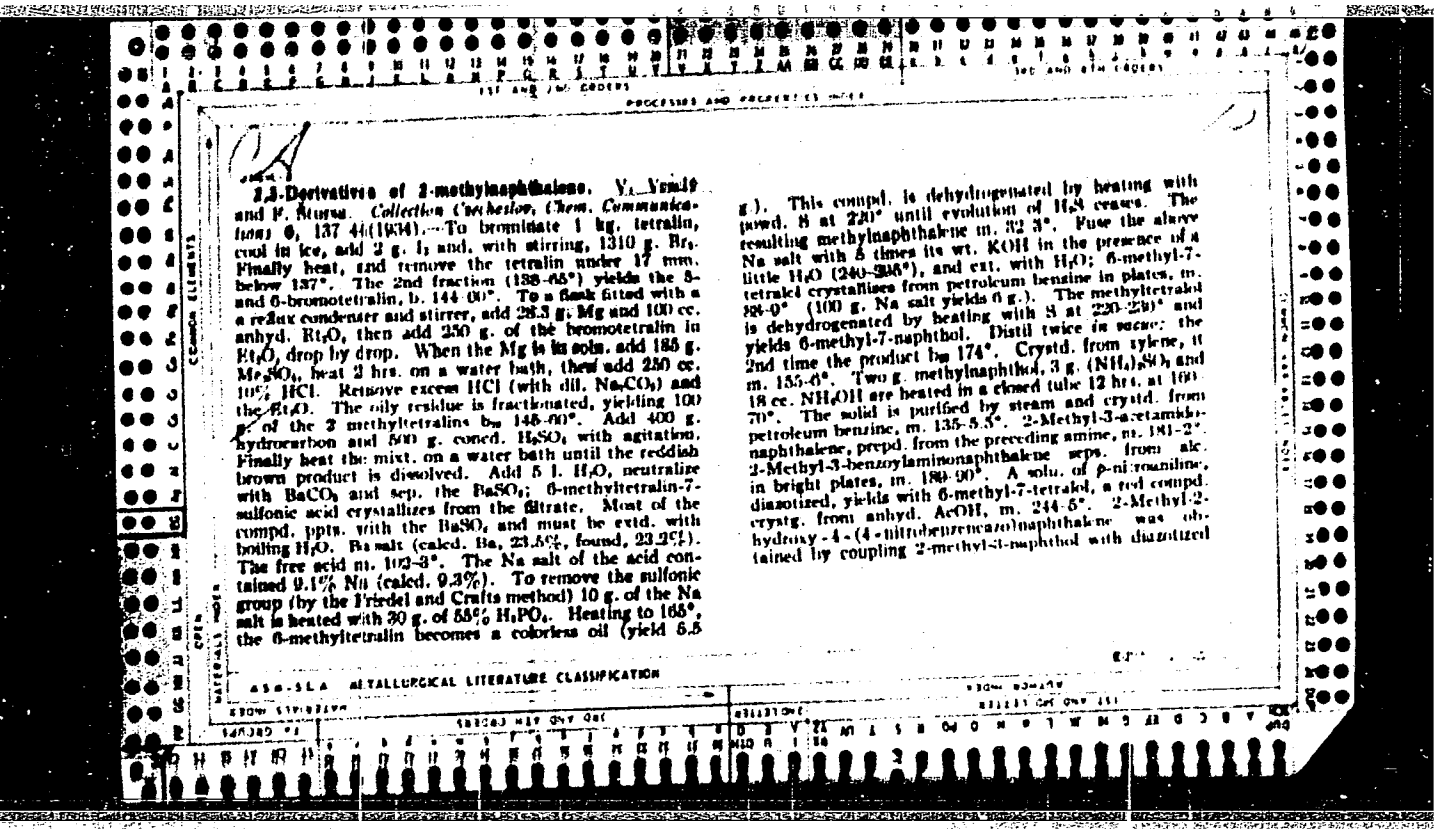
The preparation of derivatives of 1-phenylnaphthalene. V. Vesely and F. Sturm. *Collection Czechoslov. Chem. Communications* 3, 343-7(1931). Weiss and Widdich (*C. A.* 26, 1401) nitrated 1-$C_6H_5C_{10}H_7$ and obtained a product which they were led to believe was either 5- or 8-nitro-1-phenylnaphthalene. Since this was not in accord with the authors' rules for substitution in $C_{10}H_8$ (*C. A.* 18, 253) they repeated the work and came to the conclusion that W. and W.'s product was actually *4-nitro-1-phenylnaphthalene*, m. 132°. Reduction with Fe and AcOH gave *4-amino-1-phenylnaphthalene* (I), m. 73-4°. *Ac deriv.* (II), m. 167-8°. Nitration of II in AcOH gave *3-nitro-4-acetylamino-1-phenylnaphthalene*, m. 181-2°. This, reduced with $SnCl_2$, gave *3,4-diamino-1-phenylnaphthalene* (III), m. 100-1°. *1-Phenylnaphthalene-3,4-phenazine*, m. 277-228° (?) from C_6H_4N, slowly pptd. when III in alc. was refluxed with phenanthraquinone, proving III to be an *o*-diamine. *4-Bromo-1-phenylnaphthalene*, m. 76-7°, was prepd. by the Sandmeyer reaction on I in spite of W. and W.'s statement that it could not be done. John R. Milbery



The preparation of azo dyes from brominated *β*-naphthols. [illegible] and I. Sturm. *Chem. Listy* 27, 120-8(1933); a French résumé is given. Diazotized *p*-nitroaniline coupled in an alk. soln. with 1,6-dibromo-2-naphthol formed dark red plates of 2-hydroxy-6-bromo-1-[4-nitrobenzeneazo]naphthalene which, recrystd. from $PhNO_2$ and xylene, m. 272°. The same dye was prepd. from 6-bromo-2-naphthol. Diazotized *p*-nitroaniline coupled in an alk. soln. with 1,4,6-tribromo-2-naphthol, yielding 2-hydroxy-4,6-dibromo-1-[4-nitrobenzeneazo]naphthalene, delicate, dark red needles from $PhNO_2$, m. 303°, sol. in CaH_6, toluene and xylene and slightly sol. in EtOH, acetone and anhyd. AcOH. 4-Bromo-2-nitro-1-naphthylamine (15 g. in 140 cc. concd. H_2O) was cooled with ice, treated by drops with 36.8 g. nitrosylsulfuric acid, dild. with lumps of ice until complete soln. was established by the next addn. of H_2O, and left standing in 1 l. H_2O for 2 hrs. The pptd. 1,3-diazonaphth-4-bromonaphthalene (I) was filtered off and washed with CaH_6, forming 9 g. of delicate, yellow-brown needles, m. 180-1° (decompn.). Refluxing 20 g. of I in 220 cc. EtOH and 2 g. powd. Al for 24 hrs. or until a drop of the soln. failed to give a blue color with an alk. soln. of resorcinol, filtering, evapg. the EtOH, digesting the residue with dil. soda soln., and acidifying the soln. pptd. 7.4 g. of 4-bromo-2-naphthol which, washed with CaH_6 and decolorized with charcoal formed yellow needles, m. 117.5-19°. 2-Hydroxy-4-bromo-1-[4-nitrobenzeneazo]naphthalene, produced by coupling diazotized *p*-nitroaniline with 4-bromo-2-naphthol, crystd. from anhyd. AcOH in red-brown needles, m. 221-2°. On fabrics, the brominated para red dyes do not produce the bright red shades of the unbrominated dyes; all of the brominated products gave a brown to a violet shade.

Frank Marsh



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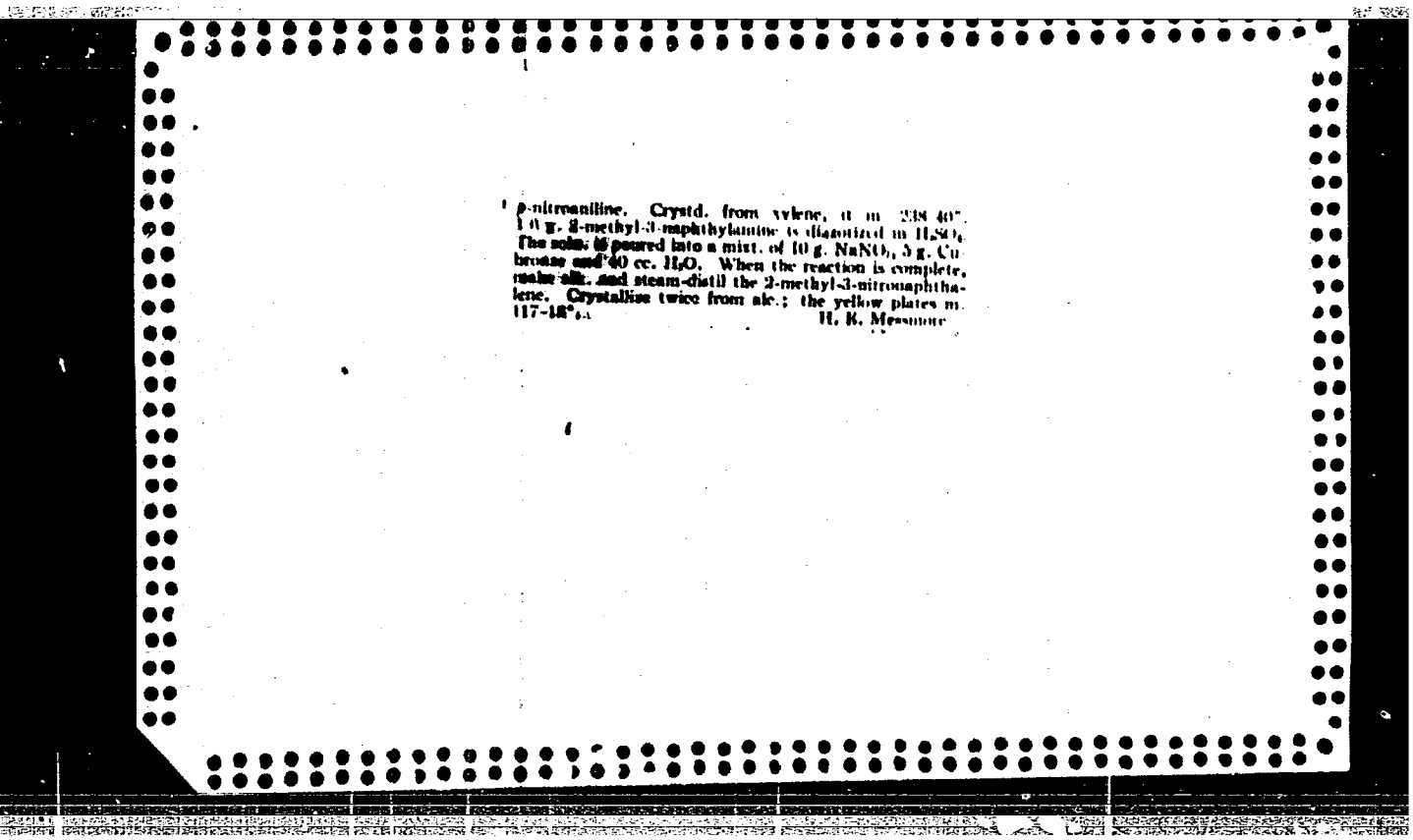
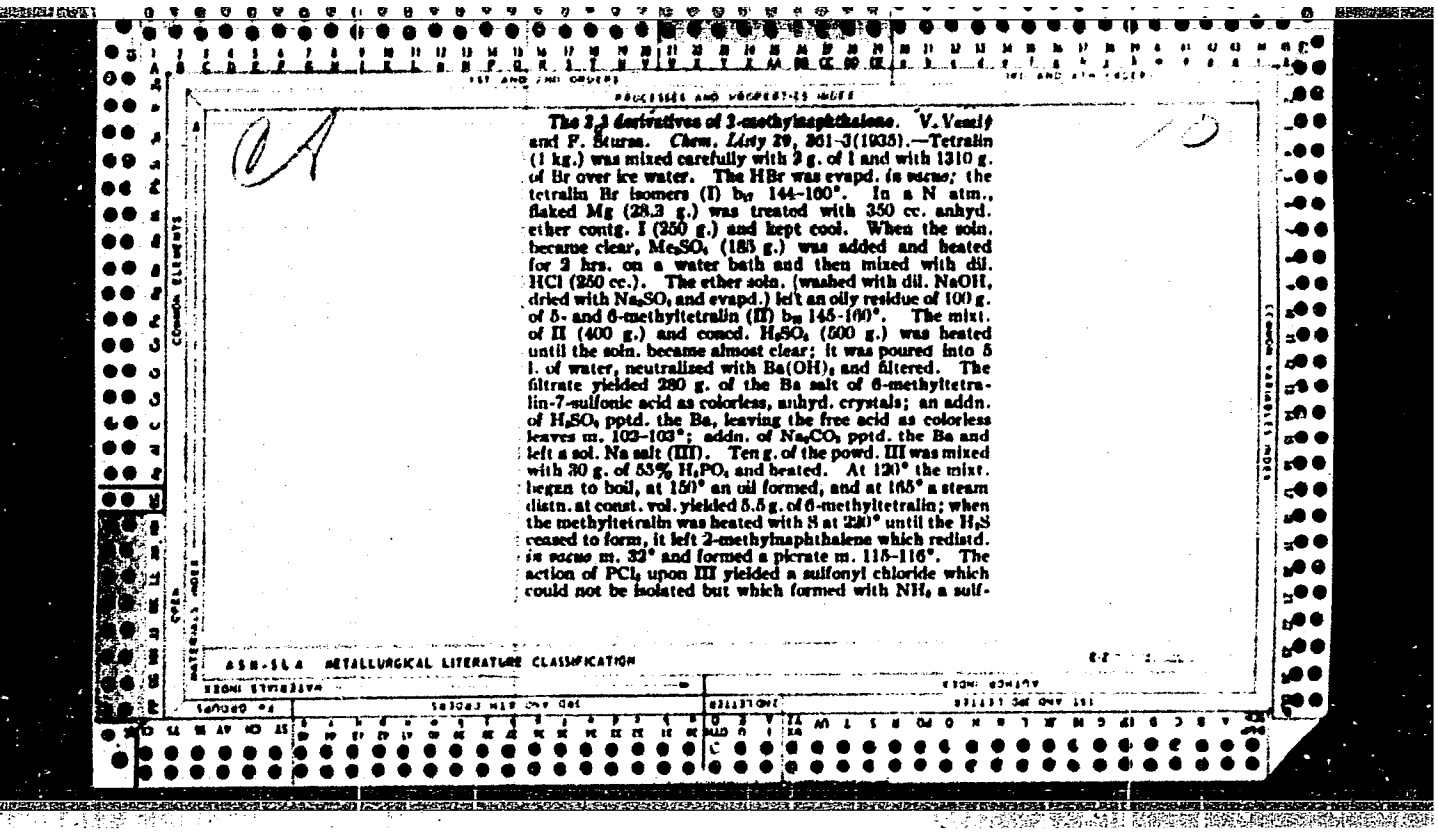
2,3-Derivatives of 2-methylnaphthalene. V. Vesely and F. Stursa. *Collection Czechoslov. Chem. Communications* 6, 137-44(1934).—To brominate 1 kg. tetralin, cool in ice, add 2 g. I_2 and, with stirring, 1310 g. Br_2. Finally heat, and remove the tetralin under 17 mm. below 137°. The 2nd fraction (138–65°) yields the 5- and 6-bromotetralin, b. 144–60°. To a flask fitted with a reflux condenser and stirrer, add 28.3 g. Mg and 100 cc. anhyd. Et_2O, then add 250 g. of the bromotetralin in Et_2O drop by drop. When the Mg is in soln. add 185 g. Me_2SO_4, heat 2 hrs. on a water bath, then add 250 cc. 10% HCl. Remove excess HCl (with dil. Na_2CO_3) and the Et_2O. The oily residue is fractionated, yielding 100 g. of the 2 methyltetralins bp 148–60°. Add 400 g. hydrocarbon and 500 g. concd. H_2SO_4 with agitation. Finally heat the mixt. on a water bath until the reddish brown product is dissolved. Add 5 l. H_2O, neutralize with $BaCO_3$ and sep. the $BaSO_4$; 6-methyltetralin-7-sulfonic acid crystallizes from the filtrate. Most of the compd. ppts. with the $BaSO_4$ and must be extd. with boiling H_2O. Ba salt (calcd. Ba, 23.5%, found, 23.2%). The free acid m. 102–3°. The Na salt of the acid contained 9.1% Na (calcd. 9.3%). To remove the sulfonic group (by the Friedel and Crafts method) 10 g. of the Na salt is heated with 30 g. of 85% H_3PO_4. Heating to 165°, the 6-methyltetralin becomes a colorless oil (yield 5.5 g.). This compd. is dehydrogenated by heating with sulfur at 220° until evolution of H_2S ceases. The resulting methylnaphthalene m. 32.5°. Fuse the above Na salt with 5 times its wt. KOH in the presence of a little H_2O (240–315°), and ext. with H_2O; 6-methyl-7-tetralol crystallizes from petroleum benzine in plates, m. 98–9° (100 g. Na salt yields 6 g.). The methyltetralol is dehydrogenated by heating with S at 220–25° and yields 6-methyl-7-naphthol. Distil twice in vacuo; the 2nd time the product bp 174°. Crystd. from xylene, it m. 155–6°. Two g. methylnaphthol, 3 g. $(NH_4)_2SO_3$ and 18 cc. NH_4OH are heated in a closed tube 12 hrs. at 100–70°. The solid is purified by steam and crystd. from petroleum benzine, m. 135–5.5°. 2-Methyl-3-acetamidonaphthalene, prepd. from the preceding amine, m. 181–2°. 2-Methyl-3-benzoylaminonaphthalene scps. from alc. in bright plates, m. 189–90°. A soln. of p-nitroaniline, diazotized, yields with 6-methyl-7-tetralol, a red compd. crystg. from anhyd. AcOH, m. 244–5°. 2-Methyl-2-hydroxy-4-(4-nitrobenzeneazo)naphthalene was obtained by coupling 2-methyl-5-naphthol with diazotized

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



p-nitroaniline. Crystd. from xylene, m. 238-40°. 10 g. 2-methyl-3-naphthylamine is diazotized in H_2SO_4. The soln. is poured into a mixt. of 10 g. $NaNO_2$, 5 g. Cu bronze and 40 cc. H_2O. When the reaction is complete, make alk. and steam-distil the 2-methyl-3-nitronaphthalene. Crystallize twice from alc.; the yellow plates m. 117-18°.

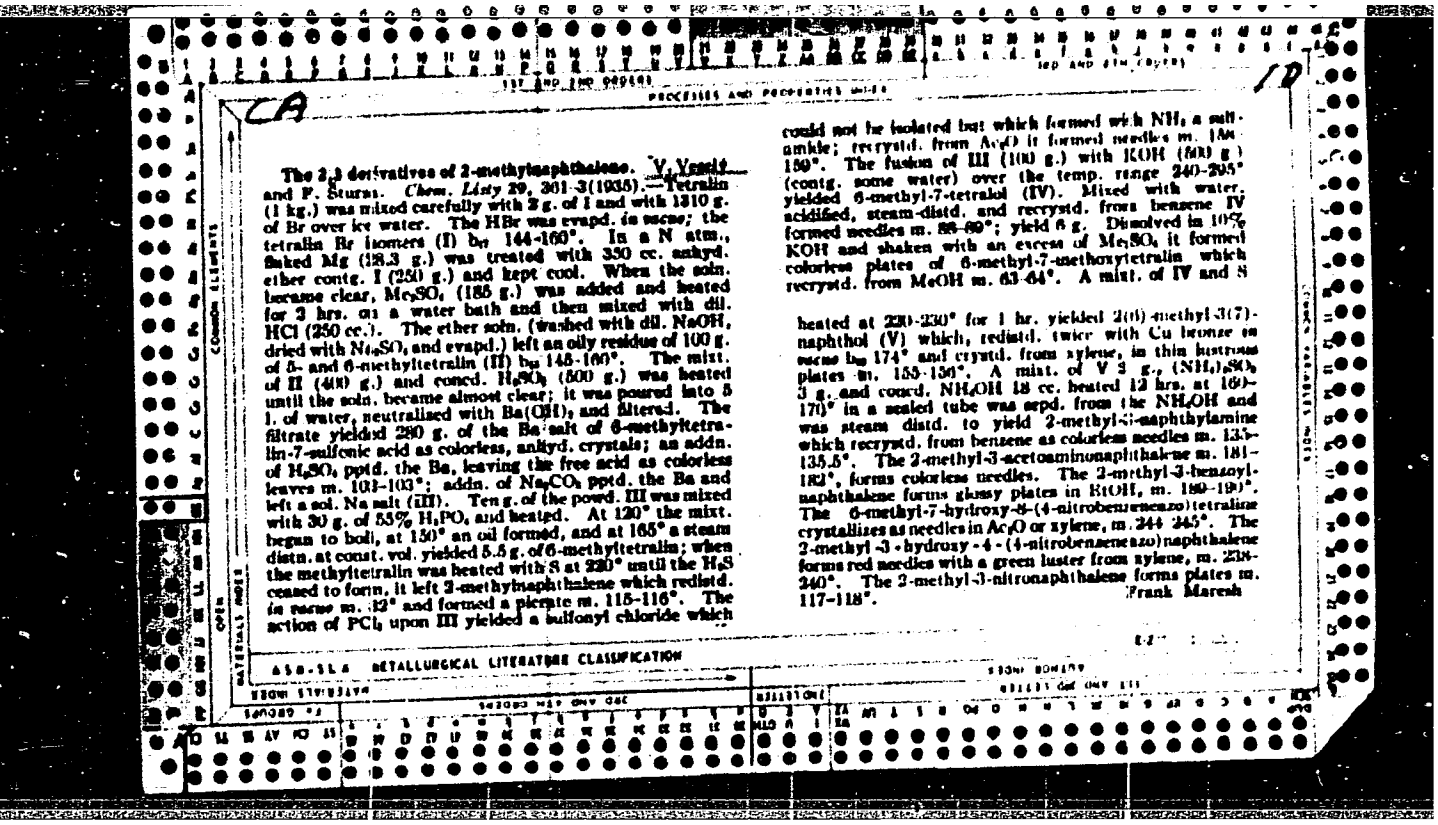
H. K. Messmore



The 2,3 derivatives of 2-methylnaphthalene. V. Vesely and F. Sturm. *Chem. Listy* 29, 361-3(1935).—Tetralin (1 kg.) was mixed carefully with 2 g. of I and with 1310 g. of Br over ice water. The HBr was evapd. *in vacuo;* the tetralin Br isomers (I) b_{12} 144–160°. In a N atm., flaked Mg (28.3 g.) was treated with 350 cc. anhyd. ether contg. I (250 g.) and kept cool. When the soln. became clear, Me_2SO_4 (185 g.) was added and heated for 2 hrs. on a water bath and then mixed with dil. HCl (250 cc.). The ether soln. (washed with dil. NaOH, dried with Na_2SO_4 and evapd.) left an oily residue of 100 g. of 5- and 6-methyltetralin (II) b_{12} 145–160°. The mixt. of II (400 g.) and concd. H_2SO_4 (500 g.) was heated until the soln. became almost clear; it was poured into 5 l. of water, neutralized with $Ba(OH)_2$ and filtered. The filtrate yielded 280 g. of the Ba salt of 6-methyltetralin-7-sulfonic acid as colorless, anhyd. crystals; an addn. of H_2SO_4 pptd. the Ba, leaving the free acid as colorless leaves m. 102–103°; addn. of Na_2CO_3 pptd. the Ba and left a sol. Na salt (III). Ten g. of the powd. III was mixed with 30 g. of 55% H_3PO_4 and heated. At 120° the mixt. began to boil, at 150° an oil formed, and at 165° a steam distn. at const. vol. yielded 5.5 g. of 6-methyltetralin; when the methyltetralin was heated with S at 220° until the H_2S ceased to form, it left 2-methylnaphthalene which redistd. *in vacuo* m. 32° and formed a picrate m. 115–116°. The action of PCl_5 upon III yielded a sulfonyl chloride which could not be isolated but which formed with NH_3 a sulf-

amide; recrystd. from Ac_2O it formed needles m. 158-159°. The fusion of III (100 g.) with KOH (500 g.) (contg. some water) over the temp. range 240-205° yielded 6-methyl-7-tetralol (IV). Mixed with water, acidified, steam-distd. and recrystd. from benzene IV formed needles m. 88-89°; yield 6 g. Dissolved in 10% KOH and shaken with an excess of Me_2SO_4 it formed colorless plates of 6-methyl-7-methoxytetralin which recrystd. from MeOH m. 63-64°. A mixt. of IV and S heated at 220-230° for 1 hr. yielded 2(6)-methyl-3(7)-naphthol (V) which, redistd. twice with Cu bronze in vacuo bp 174° and crystd. from xylene, in thin lustrous plates m. 155-156°. A mixt. of V 2 g., $(NH_4)_2SO_4$ 3 g. and concd. NH_4OH 18 cc. heated 12 hrs. at 160-170° in a sealed tube was sepd. from the NH_4OH and was steam distd. to yield 2-methyl-3-naphthylamine which recrystd. from benzene as colorless needles m. 135-135.5°. The 2-methyl-3-acetoaminonaphthalene m. 181-182°, forms colorless needles. The 2-methyl-3-benzoylnaphthalene forms glossy plates in EtOH, m. 189-190°. The 6-methyl-7-hydroxy-6-(4-nitrobenzeneazo)tetraline crystallizes as needles in Ac_2O or xylene, m. 244-245°. The 2-methyl-3-hydroxy-4-(4-nitrobenzeneazo)naphthalene forms red needles with a green luster from xylene, m. 238-240°. The 2-methyl-3-nitronaphthalene forms plates m. 117-118°.

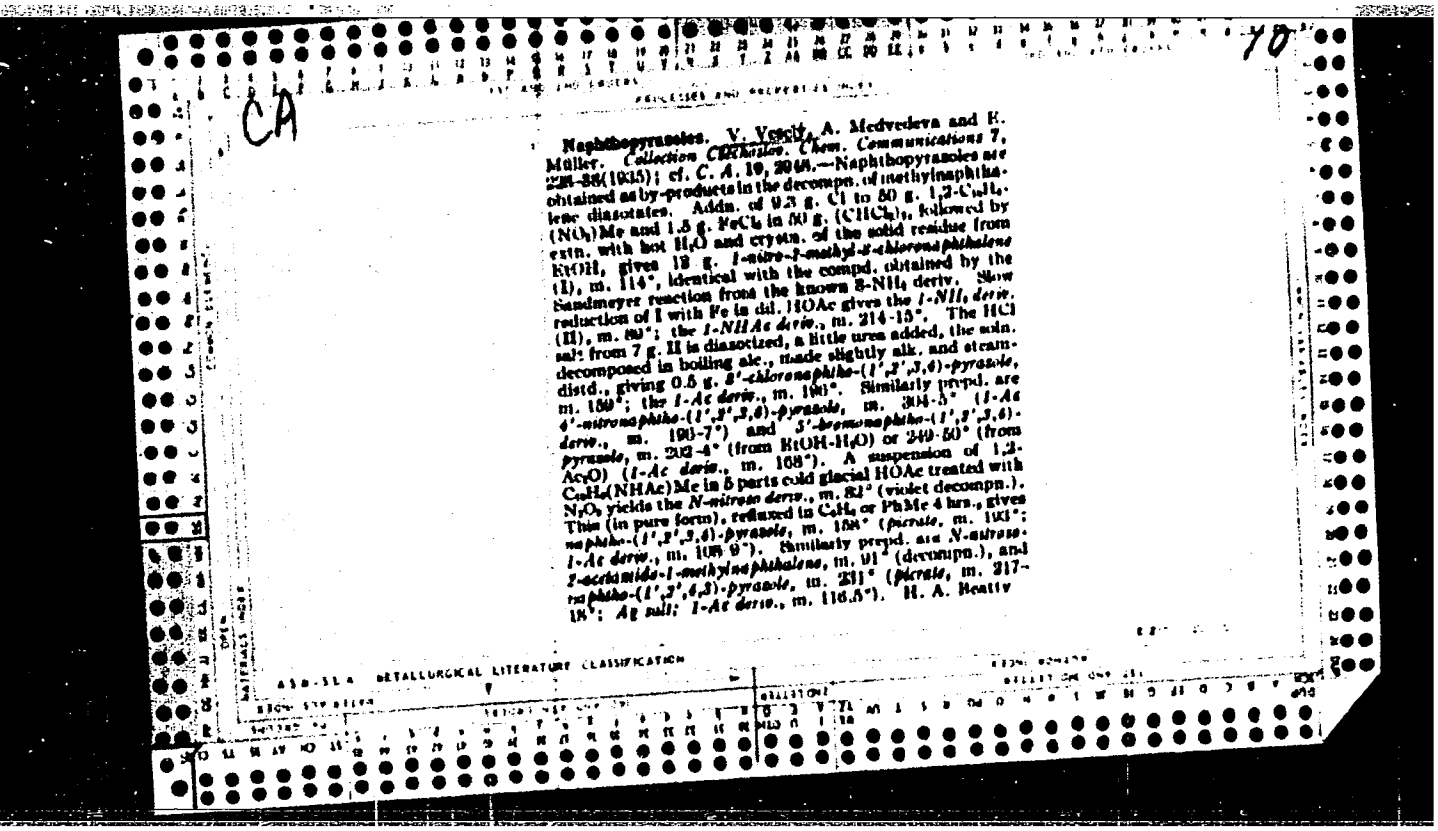
Frank Maresh



CA

The 2,3 derivatives of 2-methylnaphthalene. V. Vranić and F. Sturm. *Chem. Listy* 29, 301-3(1935).—Tetralin (1 kg.) was mixed carefully with 2 g. of I and with 1310 g. of Br over ice water. The HBr was evapd. *in vacuo*; the tetralin Br isomers (I) bp 144-160°. In a N atm., flaked Mg (128.3 g.) was treated with 350 cc. anhyd. ether contg. I (250 g.) and kept cool. When the soln. became clear, Me_2SO_4 (185 g.) was added and heated for 2 hrs. on a water bath and then mixed with dil. HCl (250 cc.). The ether soln. (washed with dil. NaOH, dried with Na_2SO_4 and evapd.) left an oily residue of 100 g. of 5- and 6-methyltetralin (II) bp 148-160°. The mixt. of II (400 g.) and concd. H_2SO_4 (500 g.) was heated until the soln. became almost clear; it was poured into 5 l. of water, neutralized with $Ba(OH)_2$ and filtered. The filtrate yielded 280 g. of the Ba salt of 6-methyltetralin-7-sulfonic acid as colorless, anhyd. crystals; an addn. of H_2SO_4 pptd. the Ba, leaving the free acid as colorless leaves m. 103-103°; addn. of Na_2CO_3 pptd. the Ba and left a sol. Na salt (III). Ten g. of the powd. III was mixed with 30 g. of 55% H_3PO_4 and heated. At 120° the mixt. began to boil, at 150° an oil formed, and at 165° a steam distn. at const. vol. yielded 5.5 g. of 6-methyltetralin; when the methyltetralin was heated with S at 220° until the H_2S ceased to form, it left 2-methylnaphthalene which redistd. *in vacuo* m. 42° and formed a picrate m. 115-116°. The action of PCl_5 upon III yielded a sulfonyl chloride which could not be isolated but which formed with NH_3 a sulfonamide; recrystd. from Ac_2O it formed needles m. 146-150°. The fusion of III (100 g.) with KOH (500 g.) (contg. some water) over the temp. range 240-295° yielded 6-methyl-7-tetralol (IV). Mixed with water, acidified, steam-distd. and recrystd. from benzene IV formed needles m. 88-89°; yield 6 g. Dissolved in 10% KOH and shaken with an excess of Me_2SO_4 it formed colorless plates of 6-methyl-7-methoxytetralin which recrystd. from MeOH m. 63-64°. A mixt. of IV and S heated at 220-230° for 1 hr. yielded 2(or)-methyl-3(7)-naphthol (V) which, redistd. twice with Cu bronze *in vacuo* bp 174° and crystd. from xylene, in thin lustrous plates m. 155-156°. A mixt. of V 3 g., $(NH_4)_2SO_3$ 3 g. and concd. NH_4OH 18 cc. heated 12 hrs. at 160-170° in a sealed tube was extd. from the NH_4OH and was steam distd. to yield 2-methyl-3-naphthylamine which recrystd. from benzene as colorless needles m. 134-135.5°. The 2-methyl-3-acetoaminonaphthalene m. 181-182°, forms colorless needles. The 2-methyl-3-benzoylnaphthalene forms glassy plates in EtOH, m. 189-190°. The 6-methyl-7-hydroxy-8-(4-nitrobenzeneazo)tetralin crystallizes as needles in Ac_2O or xylene, m. 244-245°. The 2-methyl-3-hydroxy-4-(4-nitrobenzeneazo)naphthalene forms red needles with a green luster from xylene, m. 238-240°. The 2-methyl-3-nitronaphthalene forms plates m. 117-118°.

Frank Maresh



CA

70

Naphthopyranoles. V. Vesely, A. Medvedeva and R. Müller. *Collection Czechoslov. Chem. Communications* 7, 228-38(1935); cf. *C. A.* 19, 2048.—Naphthopyranoles are obtained as by-products in the decompn. of methylnaphthalene diazotates. Addn. of 9.3 g. Cl to 50 g. 1,2-$C_{10}H_6$-$(NO_2)Me$ and 1.5 g. $FeCl_3$ in 50 g. $(CHCl_2)_2$, followed by extn. with hot H_2O and crystn. of the solid residue from EtOH, gives 13 g. *1-nitro-2-methyl-3-chloronaphthalene* (I), m. 114°, identical with the compd. obtained by the Sandmeyer reaction from the known 3-NH_2 deriv. Slow reduction of I with Fe in dil. HOAc gives the *1-NH₂ deriv.* (II), m. 80°; the *1-NHAc deriv.*, m. 214-15°. The HCl salt from 7 g. II is diazotized, a little urea added, the soln. decomposed in boiling alc., made slightly alk. and steam-distd., giving 0.5 g. *3'-chloronaphtho-(1',2',3,4)-pyranole*, m. 159°; the *1-Ac deriv.*, m. 190°. Similarly prepd. are *4'-nitronaphtho-(1',2',3,4)-pyranole*, m. 304-5° (*1-Ac deriv.*, m. 190-7°) and *5'-bromonaphtho-(1',2',3,4)-pyranole*, m. 202-4° (from EtOH-H_2O) or 249-50° (from Ac_2O) (*1-Ac deriv.*, m. 168°). A suspension of 1,2-$C_6H_3(NHAc)Me$ in 5 parts cold glacial HOAc treated with N_2O_3 yields the *N-nitroso deriv.*, m. 82° (violet decompn.). This (in pure form), refluxed in C_6H_6 or PhMe 4 hrs., gives *naphtho-(1',2',3,4)-pyranole*, m. 158° (*picrate*, m. 103°; *1-Ac deriv.*, m. 108-9°). Similarly prepd. are *N-nitroso-2-acetamido-1-methylnaphthalene*, m. 91° (decompn.), and *naphtho-(1',2',4,3)-pyranole*, m. 231° (*picrate*, m. 217-18°; *Ag salt*; *1-Ac deriv.*, m. 116.5°). H. A. Beatty

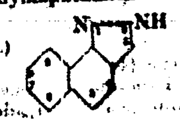
1ST AND 2ND ORDERS

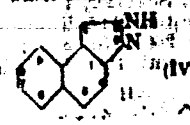
PROCESSES AND PROPERTIES INDEX

a-3

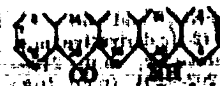
Naphthindazoles. [illegible] V. [illegible], A. [illegible], and F. Müller (Coll. Czech. Chem. Comm., [illegible], 7, [illegible]).—[illegible] 1-$C_{10}H_6$MeNO$_2$ in $(CHCl_2)_2$ with $FeCl_3$ and Cl_2 affords [illegible] m.p. 116° (also obtained (Sandmeyer) from the corresponding [illegible]-NH_2-compound), and this, when dissolved in EtOH and slowly added to [illegible] boiling AcOH-H_2O, is reduced to the amine, m.p. [illegible]° [Ac derivative (I), m.p. 214—215°]. When diazotised and poured into boiling EtOH, this amine affords some 9-chloro-α-naphthindazole (II), m.p. 159° (2:4:6- [illegible] derivative, m.p. 186°) (cf. A., 1921, [illegible]), but no 8:2-$C_{10}H_6$[illegible] could be isolated. (II) was also obtained by treating (I) in Ac_2O with N_2O_3 and boiling the resulting crude N-NO-derivative in C_6H_6 for 3 hr. (cf. A., 1908, i, 296). 4-Nitro-1-amino-2-methylnaphthalene in EtOH, when diazotised and

(III.)





(IV.)



[illegible] m.p. 403°, by heating with [illegible]. Similarly from the appropriate diaryl-aminoterephthalic acid (II) are prepared 4:8-, m.p. 347°, and 2:6-[illegible], m.p. 337°; 4:8-dimethoxy-, m.p. 318°; 1:2:5:6-dibenzo- (III) [together with a little 2-β-naphthylamino-[illegible]-3-carboxylic acid (IV) ([illegible] salt)] and 3:4:7:8-dibenzo-, m.p. 348° (dodecachlorodihydroxy derivative, m.p. 410° (decomp.)), -quinacridone. Et 2:5-di-β-naphthylamino-terephthalate and [illegible] at 150—160° afford a little (III) and the 12:14-Me_2 derivative, m.p. > 400° (decomp.), and (IV). When warmed with conc. H_2SO_4 (III) gives its disulphonic acid. By heating the appropriate (II) with K_2CO_3, [illegible], and Cu in

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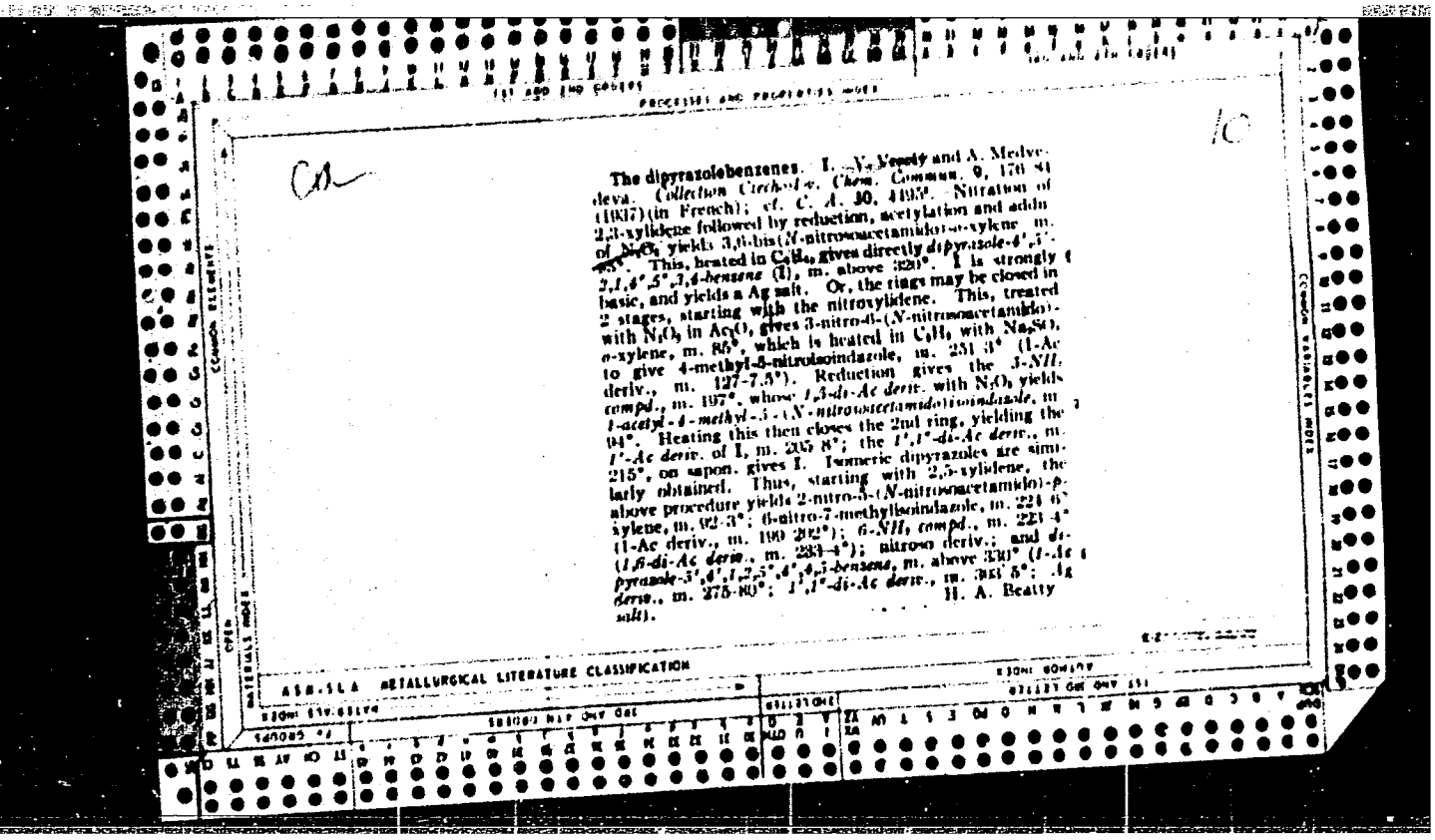
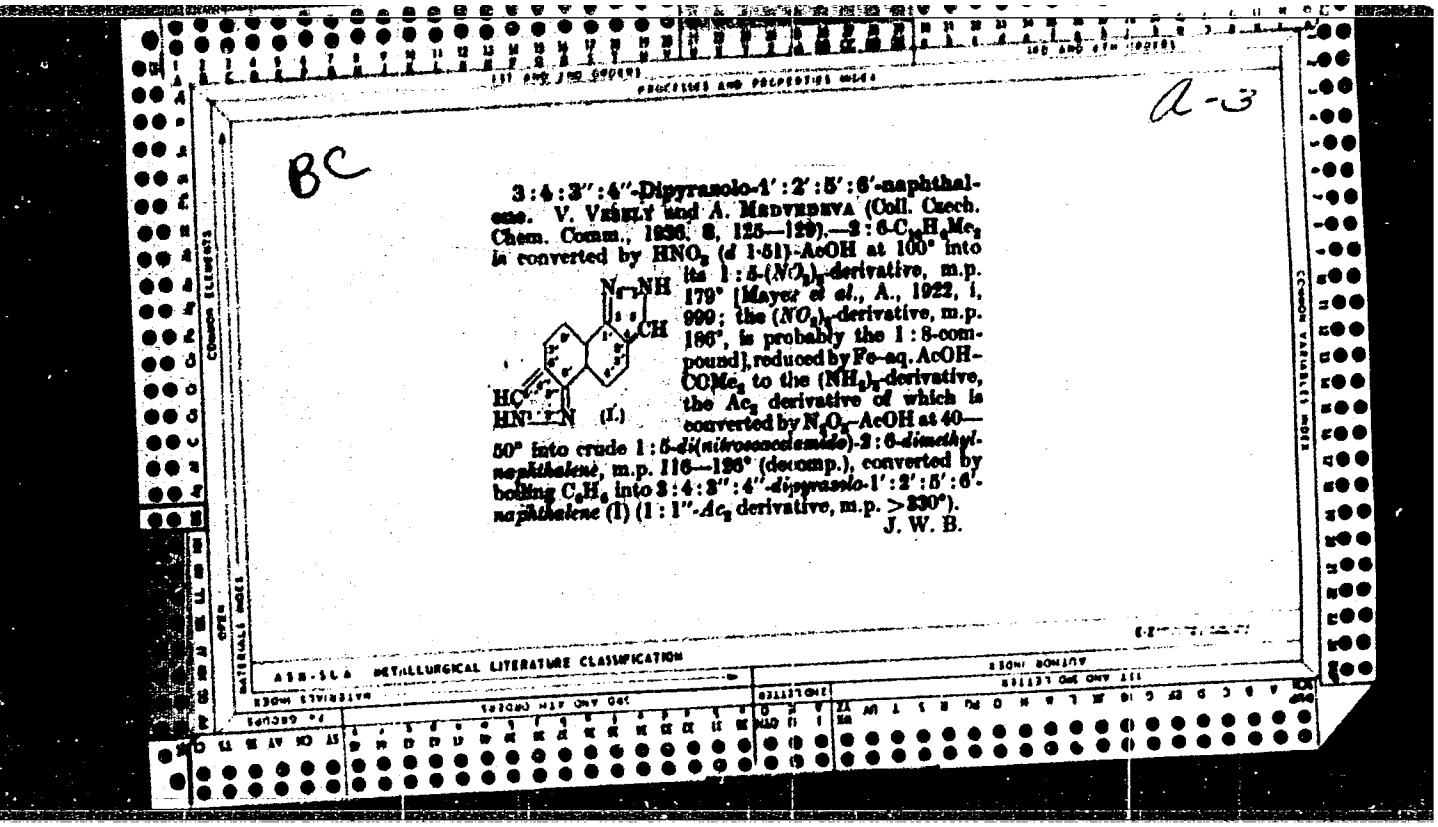


The dipyrazolobenzenes. I. V. Veselý and A. Medvedeva. *Collection Czechoslov. Chem. Communs.* 9, 170-84 (1937)(in French); cf. *C. A.* 30, 4193⁹. Nitration of 2,3-xylidene followed by reduction, acetylation and acidic yields 3,6-bis(*N*-nitrosoacetamido)-*o*-xylene, m. 165°. This, heated in C_6H_6, gives directly *dipyrazole-4',5'-2,1,6',5',3,4-benzene* (I), m. above 320°. I is strongly basic, and yields a Ag salt. Or, the rings may be closed in 2 stages, starting with the nitroxylidene. This, treated with N_2O_3 in AcOH, gives 3-nitro-6-(*N*-nitrosoacetamido)-*o*-xylene, m. 86°, which is heated in C_6H_6 with Na_2SO_4, to give 4-methyl-6-nitrosoindazole, m. 251-3° (1-Ac deriv., m. 127-7.5°). Reduction gives the 3-*NH*$_2$ *compd.*, m. 197°, whose *1,3-di-Ac deriv.* with N_2O_3 yields *1-acetyl-4-methyl-5-(N-nitrosoacetamido)indazole*, m. 104°. Heating this then closes the 2nd ring, yielding the *1'-Ac deriv.* of I, m. 205-8°; the *1',1''-di-Ac deriv.*, m. 215°, on sapon. gives I. Isomeric dipyrazoles are similarly obtained. Thus, starting with 2,5-xylidene, the above procedure yields 2-nitro-5-(*N*-nitrosoacetamido)-*p*-xylene, m. 92-3°; 6-nitro-7-methylisoindazole, m. 224-6° (1-Ac deriv., m. 190-202°); 6-*NH*$_2$ *compd.*, m. 223-4° (*1,6-di-Ac deriv.*, m. 233-4°); nitroso deriv.; and *dipyrazole-5',6',1,2,5',6',3,4-benzene*, m. above 330° (*1-Ac deriv.*, m. 275-80°; *1',1''-di-Ac deriv.*, m. 351-5°; Ag salt). H. A. Beatty



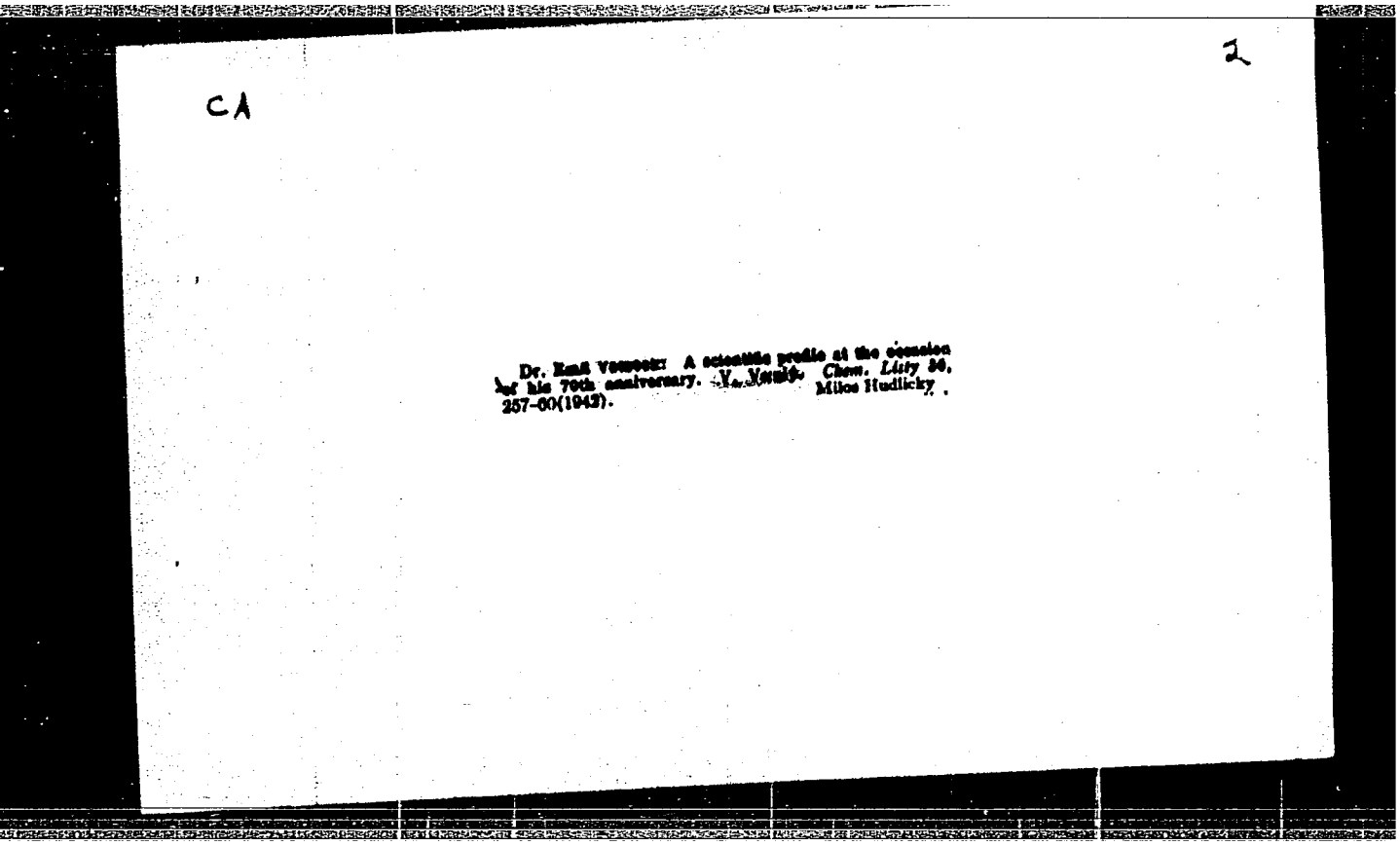
A-3

BC

3 : 4 : 3'' : 4''-Dipyranolo-1' : 2' : 5' : 6'-naphthalene. V. VEselý and A. Madverdova (Coll. Czech. Chem. Comm., 1936, 8, 125—129).—2 : 6-$C_{10}H_6Me_2$ is converted by HNO_3 (*d* 1·51)–AcOH at 100° into its 1 : 5-$(NO_2)_2$-derivative, m.p. 179° [Mayer *et al.*, A., 1922, i, 999; the $(NO_2)_2$-derivative, m.p. 166°, is probably the 1 : 8-compound], reduced by Fe–aq. AcOH–$COMe_2$ to the $(NH_2)_2$-derivative, the Ac_2 derivative of which is converted by N_2O_3–AcOH at 40—50° into crude 1 : 5-*di*(*nitrosoacetamido*)-2 : 6-*dimethylnaphthalene*, m.p. 116—126° (decomp.), converted by boiling C_6H_6 into 3 : 4 : 3'' : 4''-*dipyrano*-1' : 2' : 5' : 6'-*naphthalene* (I) (1 : 1''-Ac_2 derivative, m.p. >330°).

(I.)

J. W. B.



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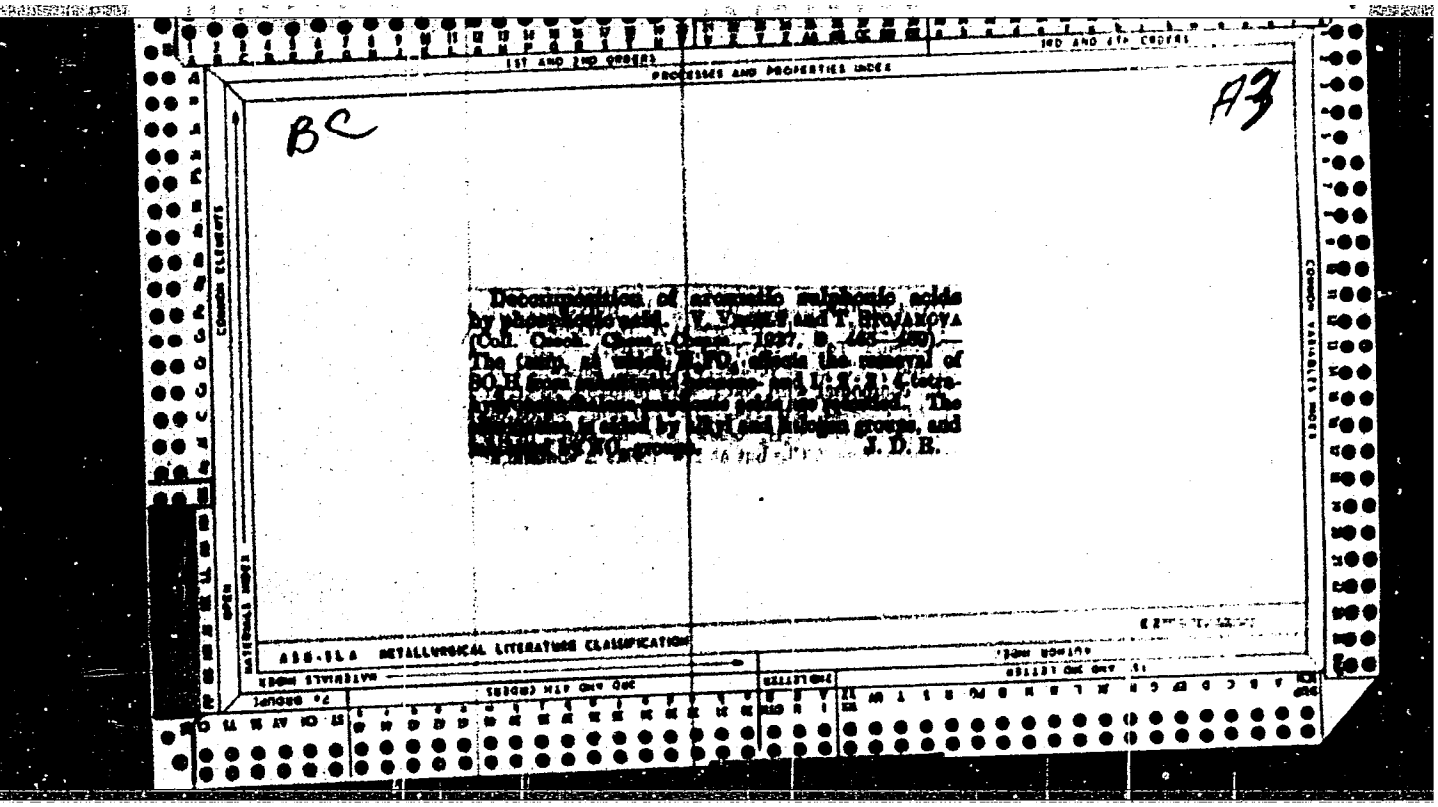
2

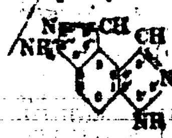
Dr. Emil Votoček: A scientific profile at the occasion of his 70th anniversary. V. Vaněk. *Chem. Listy* 36, 257-60(1942). Miloš Hudlický.



BC

J. 3

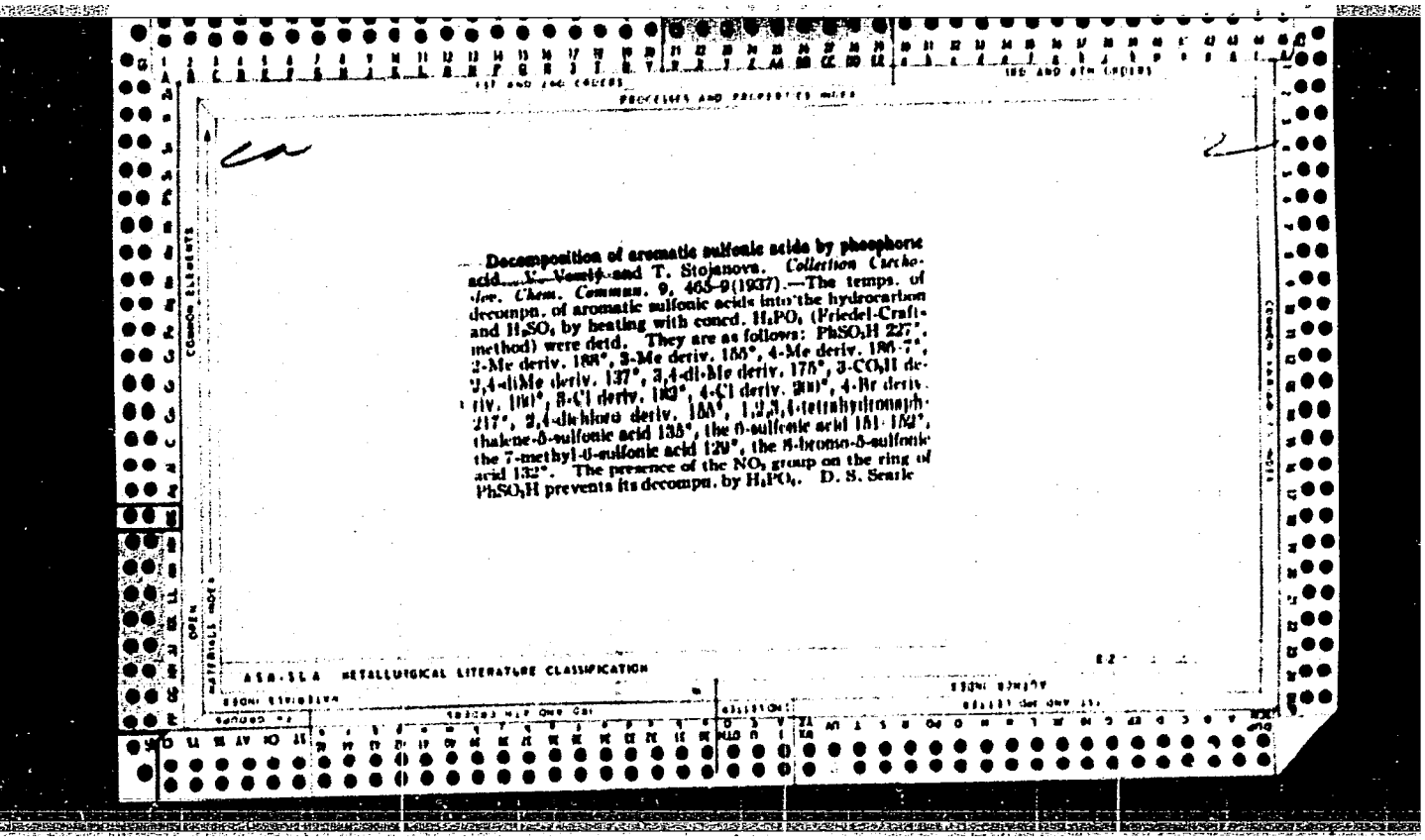
Dipyrazolobenzenes. V. Vinuš and A. Medvedeva (Coll. Czech. Chem. Comm., 1937, 9, 177—184).—4 : 1 : 2 : 3-$NO_2·C_6H_2Me_2·NHAc$ with N_2O_3 in Ac_2O gives its *NO-derivative*, m.p. 85° (decomp.), converted in boiling C_6H_6 into 6-nitro-5-methylindazole (Noelting, A., 1904, i, 689) (*Ac derivative*, m.p. 177—177.5°), reduced (Fe–AcOH) to the *6-NH_2-compound*, m.p. 197°, the *Ac_2 derivative* of which affords its 6-*NO-derivative*, m.p. 94° (decomp.), converted by boiling C_6H_6 into the 1'-*Ac derivative* (*A*; R = Ac, R' = H), sinters 205—208°, not melting completely at 325°, of 4' : 5' : 2 : 1 : 4'' : 5'' : 3 : 4-*dipyrazolobenzene* (*A*; R = R' = H), m.p. >320° (1' : 1''-*Ac_2 derivative*, m.p. 215°; *Ag salt*), obtained by hydrolysis with KOH–EtOH and also by direct decomp. of the $(NO)_2$-derivative of 1 : 2 : 3 : 6-$C_6H_2Me_2(NHAc)_2$.



(A.)

Similarly 5 : 1 : 4 : 2-$NO_2·C_6H_2Me_2·NHAc$ (improved prep.) gives a *NO-derivative*, m.p. 92—93° (decomp.), converted into 5-nitro-6-methylindazole (loc. cit.), reduced to the *5-NH_2-compound*, m.p. 228—234°, the *Ac_2 derivative*, m.p. 233—234°, of which affords a *NO-derivative*, converted into the 1'-*Ac derivative*, m.p. 275—278° (decomp.), of 5' : 4' : 1 : 2 : 5'' : 4'' : 4 : 5-*dipyrazolobenzene*, m.p. >330° (1' : 1''-*Ac_2 derivative*, m.p. 303—305°; *Ag salt*).

J. W. B.



Decomposition of aromatic sulfonic acids by phosphoric acid. V. Veselý and T. Stojanova. *Collection Czechoslov. Chem. Commun.* 9, 465–9(1937).—The temps. of decompn. of aromatic sulfonic acids into the hydrocarbon and H_2SO_4 by heating with concd. H_3PO_4 (Friedel-Crafts method) were detd. They are as follows: $PhSO_3H$ 227°, 2-Me deriv. 188°, 3-Me deriv. 155°, 4-Me deriv. 180–7°, 2,4-diMe deriv. 137°, 3,4-di-Me deriv. 175°, 3-CO_2H deriv. 191°, 3-Cl deriv. 182°, 4-Cl deriv. 200°, 4-Br deriv. 217°, 2,4-dichloro deriv. 155°, 1,2,3,4-tetrahydronaphthalene-5-sulfonic acid 135°, the 6-sulfonic acid 151–152°, the 7-methyl-6-sulfonic acid 129°, the 8-bromo-5-sulfonic acid 132°. The presence of the NO_2 group on the ring of $PhSO_3H$ prevents its decompn. by H_3PO_4. D. S. Searle

BC

H-3

Pyrazolo-tetrahydronaphthalenes. V. Veselý and T. Stojanová (Coll. Czech. Chem. Comm., 1938, 10, 142—147).—5-Acetamido-, 8-nitro-5-acetamido-, and 5:8-diacetamido-tetrahydronaphthalenes and N_2O_3 in AcOH give the N-nitrosoacetamido-derivatives, converted by boiling C_6H_6 into pyrazole-, m.p. 120—121° (Ag salt; picrate, m.p. 212—212·5°), 8-[illegible] m.p. 242° (8-NH_2-[illegible] m.p. 247—[illegible] derivative (I), m.p. [illegible], and dipyrazolo-(II), m.p. [illegible] (Ag salt; picrate, blackens at [illegible], m.p. >300°) -tetrahydronaphthalene. (I) gives similarly a nitrosoamine, converted into the 1'-acetyldipyrazole-derivative (III), m.p. >300° [1':1''-Ac_2 derivative (IV), m.p. [illegible]°]; (III) or (IV) and EtOH–KOH give (II). A. T. P.

(IV.)

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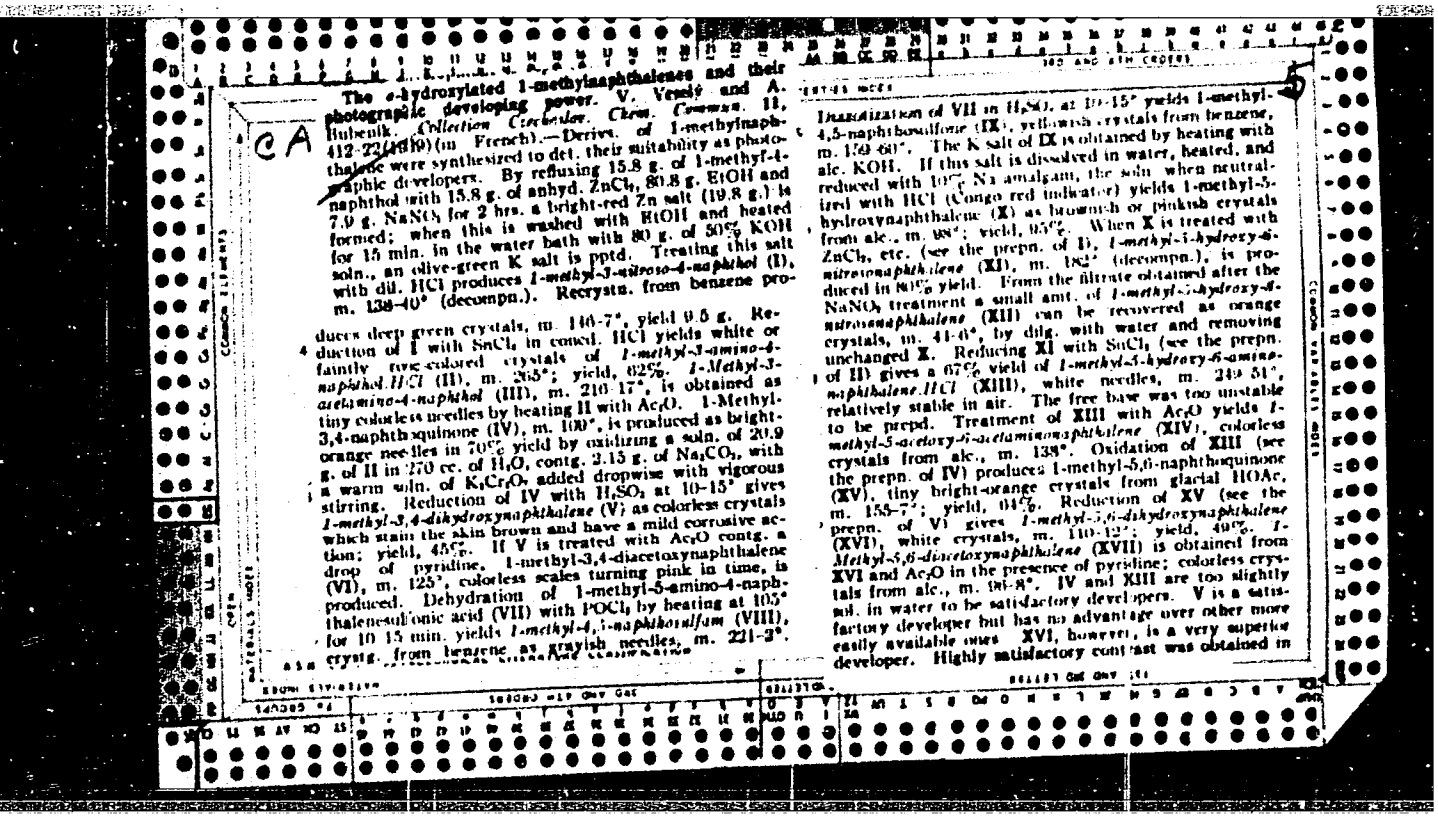

The o-hydroxylated 1-methylnaphthalenes and their photographic developing power. V. Vesely and A. Hubenik. *Collection Czechoslov. Chem. Communs.* 11, 412-22(1939)(in French).—Derivs. of 1-methylnaphthalene were synthesized to det. their suitability as photographic developers. By refluxing 15.8 g. of 1-methyl-4-naphthol with 15.8 g. of anhyd. $ZnCl_2$, 80.8 g. EtOH and 7.9 g. $NaNO_3$ for 2 hrs. a bright-red Zn salt (19.8 g.) is formed; when this is washed with EtOH and heated for 15 min. in the water bath with 80 g. of 50% KOH soln., an olive-green K salt is pptd. Treating this salt with dil. HCl produces *1-methyl-3-nitroso-4-naphthol* (I), m. 138–40° (decompn.). Recrystn. from benzene produces deep green crystals, m. 146–7°, yield 9.5 g. Reduction of I with $SnCl_2$ in concd. HCl yields white or faintly rose-colored crystals of *1-methyl-3-amino-4-naphthol.HCl* (II), m. 265°; yield, 62%. *1-Methyl-3-acetamino-4-naphthol* (III), m. 210–17°, is obtained as tiny colorless needles by heating II with Ac_2O. 1-Methyl-3,4-naphthoquinone (IV), m. 100°, is produced as bright-orange needles in 70% yield by oxidizing a soln. of 20.9 g. of II in 270 cc. of H_2O, contg. 2.15 g. of Na_2CO_3, with a warm soln. of $K_2Cr_2O_7$ added dropwise with vigorous stirring. Reduction of IV with H_2SO_3 at 10–15° gives *1-methyl-3,4-dihydroxynaphthalene* (V) as colorless crystals which stain the skin brown and have a mild corrosive action; yield, 45%. If V is treated with Ac_2O contg. a drop of pyridine, 1-methyl-3,4-diacetoxynaphthalene (VI), m. 125°, colorless scales turning pink in time, is produced. Dehydration of 1-methyl-5-amino-4-naphthalenesulfonic acid (VII) with $POCl_3$ by heating at 105° for 10–15 min. yields *1-methyl-4,5-naphthosultam* (VIII), crystg. from benzene as grayish needles, m. 221–3°. Diazotization of VII in H_2SO_4 at 10–15° yields 1-methyl-4,5-naphthosultone (IX), yellowish crystals from benzene, m. 179–80°. The K salt of IX is obtained by heating with alc. KOH. If this salt is dissolved in water, heated, and reduced with 10% Na amalgam, the soln. when neutralized with HCl (Congo red indicator) yields 1-methyl-5-hydroxynaphthalene (X) as brownish or pinkish crystals from alc., m. 98°; yield, 95%. When X is treated with $ZnCl_2$, etc. (see the prepn. of I), *1-methyl-4-hydroxy-6-nitrosonaphthalene* (XI), m. 182° (decompn.), is produced in 80% yield. From the filtrate obtained after the $NaNO_2$ treatment a small amt. of *1-methyl-4-hydroxy-6-nitrosonaphthalene* (XII) can be recovered as orange crystals, m. 41–6°, by dilg. with water and removing unchanged X. Reducing XI with $SnCl_2$ (see the prepn. of II) gives a 67% yield of *1-methyl-4-hydroxy-6-amino-naphthalene.HCl* (XIII), white needles, m. 249–51°, relatively stable in air. The free base was too unstable to be prepd. Treatment of XIII with Ac_2O yields *1-methyl-5-acetoxy-6-acetaminonaphthalene* (XIV), colorless crystals from alc., m. 138°. Oxidation of XIII (see the prepn. of IV) produces 1-methyl-5,6-naphthoquinone (XV), tiny bright-orange crystals from glacial HOAc, m. 155–7°; yield, 04%. Reduction of XV (see the prepn. of V) gives *1-methyl-5,6-dihydroxynaphthalene* (XVI), white crystals, m. 110–12°; yield, 40%. *1-Methyl-5,6-diacetoxynaphthalene* (XVII) is obtained from XVI and Ac_2O in the presence of pyridine; colorless crystals from alc., m. 98–8°. IV and XIII are too slightly sol. in water to be satisfactory developers. V is a satisfactory developer but has no advantage over other more easily available ones. XVI, however, is a very superior developer. Highly satisfactory contrast was obtained in